Reaction of Elemental Sulphur with Cobalt(II)–Schiff-base Complexes: Synthesis of μ-Disulphido and μ-Tetrasulphido Binuclear Cobalt(III) Complexes. Crystal Structures of two Binuclear Cobalt(III)–Schiff-base Complexes†

Carlo Floriani*
Chemistry Department, Columbia University, New York, N.Y. 10027, U.S.A.
Marina Fiallo
Dipartimento di Chimica e Chimica Industriale, Universitá di Pisa, 56100 Pisa, Italy
Angiola Chiesi-Villa and Carlo Guastini
Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Universita di Parma, 43100 Parma, Italy

---

Reaction of elemental sulphur with cobalt(II)–quadridentate Schiff-base complexes is reported. Elemental sulphur reacts with [Co(salphen)] [salphen = *NN′-o*-phenylenebis(salicylideneiminate)], (**1**), [Co(salen)] [salen = *NN′*-ethylenebis(salicylideneiminate)], (**2**), [Co{3,3′-(MeO)$_2$-salen}], (**3**), and [Co(α,α'-Et$_2$-salen)], (**4**), in co-ordinating solvents to afford binuclear, diamagnetic cobalt(III) complexes containing a tetrasulphido bridging ligand: [{Co(salphen)}$_2$(μ-S$_4$)L$_2$] [L = tetrahydrofuran (thf) (**5**) or pyridine (py) (**6**)]; [{Co(salen)}$_2$(μ-S$_4$)(thf)], (**7**); [{Co(salen)}$_2$(μ-S$_4$)(py)$_2$], (**8**); [{Co[3,3′-(MeO)$_2$-salen]}$_2$(μ-S$_4$)], (**9**); [{Co(α,α'-Et$_2$-salen)}$_2$(μ-S$_4$)(thf)], (**10**). Substituents on the quadridentate ligand do not affect the nature of the final compound. Carrying out the reaction of (**1**) with elemental sulphur in thf containing NaBPh$_4$ results in the formation of a completely different compound, which was isolated and structurally characterized as [{Co(salphen)}$_2$S$_2$Na(thf)$_2$]BPh$_4$, (**11**). This is a diamagnetic binuclear cobalt(III) complex, in which the two Co(salphen) units are bridged by the S_2^{2-} ligand and by the Na$^+$ which is bonded to all four oxygen atoms of the Schiff-base ligands [Co–S 2.231(7), 2.249(7); S–S 1.962(9) Å]. Both the genesis and the stability of (**11**) are dependent on Na$^+$. The complex [Co(salphen)] binds Na$^+$ in a thf solution to form a binuclear complex, [{Co(salphen)}$_2$Na(thf)$_2$]BPh$_4$, (**12**), the structure of which shows two Co(salphen) units arranged around Na$^+$ creating a cavity between the two planar units for the S$_2$ ligand. Attempts to remove Na$^+$ from (**11**) by using 18-crown-6 ether resulted in decomposition of the Co–S$_2$–Co fragment and the formation of (**5**) and (**1**). Complex (**11**) can transfer a single sulphur atom to [Fe(salen)] and PPh$_3$, or the S$_2$ unit to [V(η-C$_5$Me$_5$)$_2$], resulting in formation of (**12**). Lithium, potassium, and guanidinium cations affect the reaction of [Co(salphen)] with elemental sulphur much less than the Na$^+$. Crystallographic details for complex (**11**) are space group $P\bar{1}$ (triclinic), a = 11.816(1), b = 15.949(2), c = 17.437(2) Å, α = 93.70(1), β = 93.90(1), γ = 94.86(1)°, Z = 2, R 0.059 (R' = 0.058) for 1 479 observed reflections; and for complex (**12**) are space group *Pnna* (orthorhombic), a = 20.223(4), b = 29.197(8), c = 20.204(4) Å, Z = 8, and R 0.065 (R' = 0.069) for 1 516 observed reflections.

Sulphur–metal chemistry is largely associated with transition-metal complexes having ancillary ligands other than macrocycles or polydentate Schiff bases.[1–5] Moreover, the reaction of a transition-metal complex with elemental sulphur is not a reaction commonly employed. Such a synthetic route would be, however, very attractive in the case of metals bonded to polydentate or macrocyclic ligands. Some of the interesting features of such a reaction are as follows. (*i*) The reactivity of the sulphur–sulphur bond[6] with metals which mimic organic free radicals, carbenes, carbanions, *etc.*[7] (*ii*) Useful comparison between the reaction with molecular oxygen,[8] which is well known for metal–macrocycle complexes, and with elemental sulphur can be made. A significant parallel exists in the side-on co-ordination of O$_2$ and S$_2$ to phosphine complexes of Group 8 metals.[9] (*iii*) Disulphido, S_2^- and S_2^{2-}, ligands can be generated by free-radical type complexes, which are capable of binding O$_2$ either in the superoxo- or in the peroxo-form,[8,10] as the S–S bond is highly susceptible to free-radical attack.[6] (*iv*) The structural and chemical relationship between the MS$_2$[9] and MS$_2$M[11] fragments with the corresponding MO$_2$ and MO$_2$M units[8] in the analogous complexes.

This paper deals with the reactivity of cobalt(II)–quadridentate Schiff-base complexes, which are well known for their reactivity with molecular oxygen.[8] Binuclear cobalt(III) complexes containing a bridging tetrasulphido dianion Co–S$_4$–Co are formed by a pathway which is similar to the Schiff-base complex reaction with molecular oxygen. Such a pathway can be, for some complexes, affected significantly by the presence of alkali-metal cations in the reaction media. When [Co(salphen)] [salphen = *NN′-o*-phenylenebis(salicylideneiminate)] was treated with elemental sulphur in the presence of NaBPh$_4$, the μ-disulphido(2−) complex, [{Co(salphen)}$_2$(μ-S$_2$)Na(thf)$_2$]BPh$_4$ (thf = tetrahydrofuran) was isolated and structurally identified along with its probable precursor [{Co(salphen)}$_2$Na(thf)$_2$]BPh$_4$. Some of these results have been reported in a preliminary communication.[12]

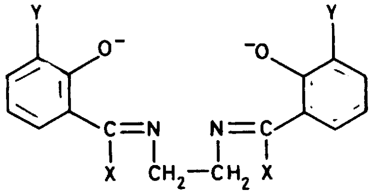
Experimental

All the reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use

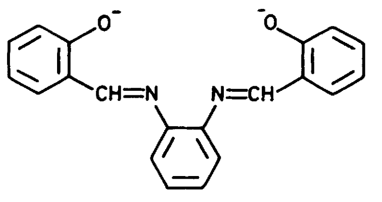
---

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

via standard techniques. I.r. spectra were recorded with a Perkin-Elmer 283 spectrophotometer. Magnetic susceptibility was determined by the Faraday method. The syntheses of [Co(salphen)],[13] (**1**), [Co(salen)],[13] (**2**), [salen = *NN'*-ethylenebis(salicylideneiminate)], [Co{3,3'-(MeO)$_2$-salen}],[14] (**3**), [Co(α,α'-Et$_2$-salen)],[14] (**4**), [Fe(salen)],[15] and [V(η-C$_5$Me$_5$)$_2$] [16] were carried out by published procedures.



X = Y = H; salen
X = H, Y = MeO; 3,3'-(MeO)$_2$-salen
X = Et, Y = H; α,α'-Et$_2$-salen



salphen

Reactions of [Co(salphen)] *with Elemental Sulphur*.—(*a*) *In thf.* A thf suspension (100 cm^3) of [Co(salphen)] (1.00 g, 2.68 mmol) was treated with crystalline S$_8$ (0.20 g, 0.78 mmol). The suspension was stirred until all the solid had dissolved. On standing at room temperature for 4 d the solution gave a black microcrystalline solid [{Co(salphen)}$_2$S$_4$(thf)$_2$], (**5**) (*ca.* 38% yield) (Found: C, 56.8; H, 4.15; N, 5.55; S, 11.9. Calc. for C$_{48}$H$_{44}$Co$_2$N$_4$O$_6$S$_4$: C, 56.6; H, 4.35; N, 5.50; S, 12.6%). Complex (**5**) is diamagnetic.

(*b*) *In pyridine.* To a pyridine (py) solution (50 cm^3) of crystalline S$_8$ (0.60 g, 2.34 mmol), solid [Co(salphen)] (3.00 g, 8.04 mmol) was added. A red solution formed suddenly. On addition of Et$_2$O (40 cm^3) the solution gave a microcrystalline red solid complex [{Co(salphen)}$_2$S$_4$(py)$_2$], (**6**). The solid was filtered off, washed well with Et$_2$O, and dried for 2 d at 120 °C (*ca.* 53% yield) (Found: C, 57.35; H, 3.60; N, 8.15; S, 13.2. Calc. for C$_{50}$H$_{38}$Co$_2$N$_6$O$_4$S$_4$: C, 58.15; H, 3.70; N, 8.15; S, 12.9%).

(*c*) *In the presence of* LiBPh$_4$. To a thf suspension (50 cm^3) of [Co(salphen)] (1.00 g, 2.68 mmol), LiBPh$_4$ (0.805 g, 2.47 mmol) and S$_8$ (0.20 g, 0.78 mmol) were added. The suspension was stirred until almost all the solid had dissolved. Undissolved solid particles were filtered off. The solution, on standing for 2 d, gave a violet crystalline solid, [{Co(salphen)S$_2$(thf)}$_2$Li]BPh$_4$, (**15**) (*ca.* 79% yield) (Found: C, 63.75; H, 4.10; Co, 8.75; N, 4.35; S, 9.55. Calc. for C$_{72}$H$_{64}$BCo$_2$LiN$_4$O$_6$S$_4$: C, 64.25; H, 4.80; Co, 8.75; N, 4.15; S, 9.55%).

(*d*) *In the presence of* NaBPh$_4$. The compound [Co(salphen)] (1.00 g, 2.68 mmol) was added to a thf solution (200 cm^3) of NaBPh$_4$ (4.00 g, 11.70 mmol). The suspension was stirred for 30 min resulting in a red solution, which was treated with crystalline S$_8$ (0.20 g, 0.78 mmol). The solution was stirred until all the sulphur dissolved, then Et$_2$O (50 cm^3) was added. After standing overnight, the solution gave a black crystalline solid [{Co(salphen)}$_2$S$_2$Na(thf)$_2$]BPh$_4$, (**11**) (*ca.* 74% yield) (Found: C, 66.45; H, 4.95; Co, 8.80; N, 4.15; S, 4.75. Calc. for C$_{72}$H$_{64}$BCo$_2$N$_4$NaO$_6$S$_2$: C, 66.65; H, 5.00; Co, 9.10; N, 4.30; S, 4.95%). Complex (**11**) is diamagnetic.

(*e*) *In the presence of* KBPh$_4$. To a thf suspension (50 cm^3) of [Co(salphen)], KBPh$_4$ (0.60 g, 1.68 mmol) was added, followed by addition of elemental sulphur (0.20 g, 0.78 mmol). The suspension was stirred until a homogeneous solution was obtained. Then, Et$_2$O (15 cm^3) was added, and the resulting solution gave, on standing for 4 d, a black crystalline solid, [{Co(salphen)S$_2$(thf)}$_3$K]BPh$_4$, (**16**) (*ca.* 63% yield) (Found: C, 60.85; H, 4.10; N, 4.00; S, 9.85. Calc. for C$_{96}$H$_{86}$BCo$_3$KN$_6$O$_9$S$_6$: C, 61.1; H, 4.60; N, 4.45; S, 10.2%). Complex (**16**) is diamagnetic.

(*f*) *In the presence of* [C(NH$_2$)$_3$]BPh$_4$. A thf suspension (50 cm^3) of [Co(salphen)] (1.00 g, 2.67 mmol) was stirred with [C(NH$_2$)$_3$]BPh$_4$ (1.00 g, 2.64 mmol) and S$_8$ (0.20 g, 0.78 mmol) until an homogeneous solution formed, which gave, on standing overnight, a black crystalline solid [{Co(salphen)S$_2$(thf)}$_3$C(NH$_2$)$_3$]BPh$_4$, (**17**) (*ca.* 66% yield) (Found: C, 60.5; H, 4.60; N, 6.35; S, 10.4. Calc. for C$_{97}$H$_{92}$BCo$_3$N$_9$O$_9$S$_6$: C, 61.05; H, 4.85; N, 6.60; S, 10.1%). Complex (**17**) is diamagnetic.

Reaction of [Co(salen)] *with Elemental Sulphur*.—(*a*) *In thf.* A thf suspension (100 cm^3) of [Co(salen)] (1.00 g, 3.06 mmol) was treated with S$_8$ (0.20 g, 0.78 mmol). The suspension, which suddenly became deep red upon addition of the sulphur, was stirred for 5 d. The microcrystalline solid, [{Co(salen)}$_2$S$_4$(thf)], (**7**), collected after stirring, was filtered off and dried *in vacuo* (*ca.* 57% yield) (Found: C, 50.6; H, 4.25; Co, 13.0; N, 6.45; S, 15.0. Calc. for C$_{36}$H$_{36}$Co$_2$N$_4$O$_5$S$_4$: C, 50.8; H, 4.25; Co, 13.85; N, 6.60; S, 15.05%).

(*b*) *In pyridine.* The reaction was carried out as reported for complex (**6**) to yield [{Co(salen)}$_2$S$_4$(py)$_2$] (**8**) (Found: C, 53.6; H, 4.35; N, 8.55; S, 13.4. Calc. for C$_{42}$H$_{38}$Co$_2$N$_6$O$_4$S$_4$: C, 53.85; H, 4.10; N, 8.95; S, 13.7%). Complexes (**7**) and (**8**) are diamagnetic.

Reaction of [Co{3,3'-(MeO)$_2$-salen}] *with Elemental Sulphur in thf.*—A thf suspension (50 cm^3) of [Co{3,3'-(MeO)$_2$-salen}] (1.00 g, 2.65 mmol) was treated with S$_8$ (0.20 g, 0.78 mmol). The red solution darkened immediately. The reaction mixture was stirred for 4 d. A black-violet solid formed, [{Co[3,3'-(MeO)$_2$-salen]}$_2$S$_4$], (**9**), and was filtered from solution and dried *in vacuo* (*ca.* 79% yield) (Found: C, 48.0; H, 3.95; N, 5.90; S, 14.5. Calc. for C$_{36}$H$_{36}$Co$_2$N$_4$O$_8$S$_4$: C, 48.1; H, 4.05; N, 6.25; S, 14.25%). Complex (**9**) is diamagnetic.

Reaction of [Co(α,α'-Et$_2$-salen)] *with Elemental Sulphur in thf.*—A thf suspension (50 cm^3) of [Co(α,α'-Et$_2$-salen)] was treated with S$_8$ (0.20 g, 0.78 mmol). The suspension became dark red within a few minutes and a microcrystalline black solid started to form. After 2 d the black solid [{Co(α,α'-Et$_2$-salen)}$_2$S$_4$(thf)], (**10**), was filtered off and dried *in vacuo* (*ca.* 72% yield) (Found: C, 52.0; H, 4.95; N, 5.80; S, 14.95. Calc. for C$_{44}$H$_{52}$Co$_2$N$_4$O$_5$S$_4$: C, 53.95; H, 5.00; N, 6.30; S, 14.4%).

Reactions of [{Co(salphen)}$_2$S$_2$Na(thf)$_2$]BPh$_4$, (**11**).—*With triphenylphosphine.* A thf suspension (50 cm^3) of complex (**11**) was treated with PPh$_3$ (0.60 g, 2.29 mmol) and stirred until dissolution of all the solid. Diethyl ether (40 cm^3) was added which gave, on standing overnight, a crystalline solid [{Co(salphen)}$_2$Na(thf)$_2$]BPh$_4$, (**12**) (*ca.* 83% yield). The solution from which complex (**12**) was removed was evaporated to dryness and the residue extracted with refluxing benzene (20 cm^3). The benzene solution when evaporated gave a white-grey residue (*ca.* 90% yield) of PPh$_3$S (m.p. 157.5 °C).

With 18-*crown*-6. A thf (50 cm^3) solution containing complex (**11**) (0.87 g, 0.67 mmol) and 18-crown-6 (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclo-octadecane) (0.18 g, 0.68 mmol) was left standing for 3 d. A microcrystalline solid formed (*ca.* 64% yield) which was identified as complex (**5**).

With [Fe(salen)]. The compound [Fe(salen)] (0.71 g, 2.20 mmol) was dissolved in a thf (50 cm^3) solution of NaBPh$_4$ (1.20

Table 1. Crystal data and summary of intensity data collection and structure refinement for complexes (**11**) and (**12**)[a]

	(**11**)	(**12**)
	$C_{72}H_{64}BCo_2N_4NaO_6S_2$	$C_{72}H_{64}BCo_2N_4NaO_6$
M	1 297.1	1 233.0
a/Å	11.816(1)	20.223(4)
b/Å	15.949(2)	29.197(8)
c/Å	17.437(2)	20.204(4)
α/°	93.70(1)	90
β/°	93.90(1)	90
γ/°	94.86(1)	90
U/Å^3	3 176.8(6)	11 929(1)
Z	2	8
D_c/g cm^{-3}	1.356	1.373
Space group	$P\bar{1}$	$Pnna$ (D^6_{2h}, no. 52)[b]
Max. crystal dimensions/mm	0.05 × 0.18 × 0.34	0.18 × 0.29 × 0.64
μ/cm^{-1}	6.44	6.18
A[c]	1.02—1.20	1.10—1.40
Reflections measured	$\pm h, \pm k, l$	h, k, l
Unique data	6 229	4 794
Unique observed data (N_o) [$I > 2\sigma(I)$]	1 479	1 516
No. parameters varied (N_v)	253	290
$R(=\Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert)$	0.059	0.065
$R'(=\Sigma w^{\frac{1}{2}}\lvert F\rvert/\Sigma w^{\frac{1}{2}}\lvert F_o\rvert)$	0.058	0.069
g.o.f.[d]	0.58	0.30
$N_o:N_v$	5.9	5.2

[a] Unit-cell parameters were obtained by least-squares refinement of the setting angles of 20 carefully centred reflections chosen from diverse regions of reciprocal space. Features common to both compounds: niobium-filtered Mo-K_α radiation (λ = 0.7107 Å); Siemens AED diffractometer; θ—2θ scan mode; scan speed 3—12° min^{-1}, scan width $\theta - 0.5$ to $\theta + (0.5 + \Delta\theta)$° $\{\Delta\theta = [(\lambda_{\alpha_2} - \lambda_{\alpha_1})/\lambda] \tan\theta\}$; 2$\theta$ range 5—44°. [b] Systematic absences: $0kl$: $k + l = 2n$; $h0l$: $l + h = 2n$; $hk0$: $h = 2n$. [c] A minimum and maximum for absorption correction factor. [d] Refined as $[\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(N_o - N_v)]^{\frac{1}{2}}$, where N_o is the number of observations and N_v the number of refined parameters.

g, 3.51 mmol) and treated with complex (**11**). A week later [{Fe(salen)}$_2$S] crystallized (0.10 g). After limited concentration, [{Fe(salen)}$_2$S(NaBPh$_4$)(thf)$_2$][17] (0.45 g) crystallized from solution (Found: C, 65.3; H, 5.55; N, 4.40; S, 2.60. Calc. for $C_{64}H_{64}BFe_2N_4NaO_6S$: C, 66.1; H, 5.55; N, 4.80; S, 2.75%). On addition of Et$_2$O (65 cm^3) a further amount of [{Fe(salen)}$_2$S(NaBPh$_4$)(thf)$_2$] was recovered (0.3 g). The solution was concentrated, then Et$_2$O (20 cm^3) added, and crystals of complex (**12**) were formed (0.12 g).

With [V(η-C$_5$Me$_5$)$_2$]. A thf solution (50 cm^3) of complex (**11**) (1.04 g, 0.80 mmol) was treated with [V(η-C$_5$Me$_5$)$_2$] (0.34 g, 1.06 mmol). A very small amount of solid was filtered off. Complex (**12**) crystallized (0.72 g) upon addition of Et$_2$O (20 cm^3). The remaining solution was evaporated to dryness and the residue recovered with hot n-hexane (30 cm^3). The solution was filtered while hot to remove undissolved material, and after standing overnight at −30 °C black needles of [{V(η-C$_5$Me$_5$)$_2$}S$_2$] formed.

Reaction of [Co(salphen)] *with* NaBPh$_4$.—To a thf (50 cm^3) suspension of [Co(salphen)] (1.50 g, 4.00 mmol), NaBPh$_4$ (1.50 g, 4.39 mmol) was added as a solid. Upon standing for 25 min a solution was obtained, which, on addition of Et$_2$O (20 cm^3) resulted in the formation of a red-violet crystalline solid [{Co(salphen)}$_2$Na(thf)$_2$]BPh$_4$, (**12**) (*ca.* 47% yield) (Found: C, 69.25; H, 5.50; N, 4.80. Calc. for $C_{72}H_{64}BCo_2N_4NaO_6$: C, 69.6; H, 5.15; N, 4.50%).

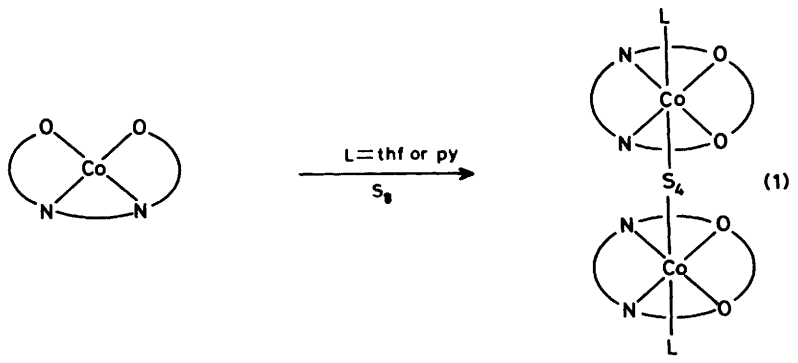
X-*Ray Crystallography for Complexes* (**11**) *and* (**12**).—Data reduction, structure solution, and refinement were carried out on a CYBER 7600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale using SHELX 76.[18] The crystals available for the *X*-ray analysis were poorly diffracting fragments of irregular shape. They were sealed in glass capillaries under nitrogen and mounted in a random orientation on a single-crystal diffractometer. The reduced cells were obtained using TRACER.[19] Crystal data and details of the parameters associated with data collection are given in Table 1. Intensity data were collected at room temperature using the profile measurement technique.[20] The structure amplitudes were obtained after the usual Lorentz and polarization reduction. No correction for absorption was applied in view of the rather low absorbance effects of the samples (Table 1).

Structure solution and refinement were based on the observed reflections. The structures were solved by the heavy-atom method. Patterson and Fourier-syntheses refinements were by full-matrix least squares, minimizing the function $\Sigma w\lvert\Delta F\rvert^2$. The weighting scheme used was $w = k/[\sigma^2(F_o) + gF_o^2]$. At convergence the values for k and g were 0.382 1, 0.004 4 respectively for the sulphur-containing complex (**11**) and 0.285 1, 0.023 34 respectively for complex (**12**). Scattering factors were taken from ref. 21 for non-hydrogen atoms and from ref. 22 for hydrogen atoms. Anomalous scattering corrections[21b] were included in all structure-factor calculations. Among the low-angle reflections no correction for secondary extinction was deemed necessary. Owing to the low percentage of reflections observed for the two compounds all the aromatic rings were considered as rigid groups having D_{6h} symmetry (C–C 1.39 Å) and only the cobalt and sulphur atoms for (**11**), and the cobalt, sodium, oxygen, and nitrogen atoms for (**12**) were allowed to vary anisotropically. The hydrogen atoms were introduced at idealized positions as fixed contributors prior to final refinement with the isotropic thermal parameters, B, fixed at 6.3 Å^2. Refinements were continued until shifts in all parameters were less than 0.3 times the standard deviation in the relevant parameter. The final difference maps showed no unusual features, with no peak above the general background of *ca.* 0.3—0.4 e Å^{-3}.

Final atomic co-ordinates are listed in Tables 2 and 3.

Table 2. Fractional atomic co-ordinates (× 10^4) for $[\{Co(salphen)\}_2(\mu-S_2)Na(thf)_2]BPh_4$, (**11**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Co	7 208(3)	1 621(2)	3 903(2)
Co	4 819(3)	2 309(2)	1 607(2)
S	5 589(6)	1 172(4)	3 204(4)
S′	5 740(6)	1 236(4)	2 095(3)
Na	6 638(8)	3 219(6)	2 937(5)
O(1)	8 005(12)	2 177(9)	3 154(8)
O(2)	6 824(12)	2 736(9)	4 193(8)
O(1′)	4 661(12)	2 905(9)	2 560(8)
O(2′)	6 141(12)	3 074(9)	1 612(8)
N(1)	7 740(15)	548(11)	3 653(10)
N(2)	6 658(15)	1 121(11)	4 760(10)
N(1′)	3 445(15)	1 611(11)	1 618(10)
N(2′)	4 922(16)	1 771(11)	640(10)
O(1A)	7 707(16)	4 512(12)	3 256(10)
C(2A)	7 591(25)	5 375(20)	3 105(17)
C(3A)	8 149(30)	5 875(22)	3 806(21)
C(4A)	8 858(30)	5 342(23)	4 258(20)
C(5A)	8 698(28)	4 531(20)	3 812(18)
O(1B)	3 857(17)	3 324(13)	1 091(12)
C(2B)	3 046(48)	3 252(32)	531(30)
C(3B)	2 605(51)	4 007(42)	352(31)
C(4B)	3 355(47)	4 647(30)	805(30)
C(5B)	4 126(38)	4 240(31)	1 321(24)
C(1)	8 577(12)	1 844(10)	2 603(8)
C(2)	8 989(12)	2 368(10)	2 045(8)
C(3)	9 555(12)	2 011(10)	1 442(8)
C(4)	9 709(12)	1 130(10)	1 396(8)
C(5)	9 297(12)	606(10)	1 953(8)
C(6)	8 731(12)	963(10)	2 557(8)
C(7)	8 335(20)	305(14)	3 073(13)
C(8)	7 362(12)	−115(9)	4 139(7)
C(9)	7 559(12)	−988(9)	4 081(7)
C(10)	7 188(12)	−1 530(9)	4 638(7)
C(11)	6 620(12)	−1 199(9)	5 252(7)
C(12)	6 423(12)	−326(9)	5 309(7)
C(13)	6 794(12)	216(9)	4 753(7)
C(14)	6 178(18)	1 480(13)	5 318(12)
C(15)	5 948(13)	2 408(7)	5 367(9)
C(16)	5 406(13)	2 715(7)	6 002(9)
C(17)	5 224(13)	3 589(7)	6 096(9)
C(18)	5 583(13)	4 156(7)	5 555(9)
C(19)	6 124(13)	3 848(7)	4 919(9)
C(20)	6 307(13)	2 974(7)	4 825(9)
C(1′)	3 754(12)	2 817(10)	2 978(8)
C(2′)	3 788(12)	3 365(10)	3 646(8)
C(3′)	2 857(12)	3 348(10)	4 097(8)
C(4′)	1 891(12)	2 782(10)	3 880(8)
C(5′)	1 857(12)	2 234(10)	3 212(8)
C(6′)	2 789(12)	2 251(10)	2 761(8)
C(7′)	2 675(19)	1 626(14)	2 092(12)
C(8′)	3 299(14)	969(9)	956(7)
C(9′)	2 445(14)	287(9)	844(7)
C(10′)	2 359(14)	−256(9)	170(7)
C(11′)	3 125(14)	−115(9)	−393(7)
C(12′)	3 978(14)	567(9)	−281(7)
C(13′)	4 065(14)	1 109(9)	393(7)
C(14′)	5 691(21)	1 954(14)	166(13)
C(15′)	6 624(12)	2 652(8)	340(11)
C(16′)	7 334(12)	2 796(8)	−254(11)
C(17′)	8 178(12)	3 486(8)	−176(11)
C(18′)	8 313(12)	4 031(8)	497(11)
C(19′)	7 603(12)	3 887(8)	1 092(11)
C(20′)	6 758(12)	3 197(8)	1 014(11)
B	8 747(24)	2 478(18)	7 301(15)
C(1E)	9 025(13)	2 121(11)	6 422(7)
C(2E)	9 022(13)	2 658(11)	5 811(7)
C(3E)	9 303(13)	2 346(11)	5 087(7)
C(4E)	9 587(13)	1 497(11)	4 973(7)
C(5E)	9 590(13)	960(11)	5 583(7)
C(6E)	9 309(13)	1 271(11)	6 308(7)
C(1F)	7 467(11)	2 083(12)	7 519(9)
C(2F)	7 202(11)	1 193(12)	7 374(9)
C(3F)	6 134(11)	817(12)	7 527(9)
C(4F)	5 333(11)	1 329(12)	7 827(9)
C(5F)	5 599(11)	2 219(12)	7 972(9)
C(6F)	6 666(11)	2 595(12)	7 819(9)
C(1C)	8 820(16)	3 583(7)	7 400(10)
C(2C)	9 587(16)	4 101(7)	7 914(10)
C(3C)	9 559(16)	4 998(7)	7 960(10)
C(4C)	8 766(16)	5 377(7)	7 492(10)
C(5C)	7 999(16)	4 859(7)	6 978(10)
C(6C)	8 026(16)	3 963(7)	6 932(10)
C(1D)	9 777(13)	2 165(9)	7 909(9)
C(2D)	9 524(13)	1 821(9)	8 603(9)
C(3D)	10 398(13)	1 588(9)	9 105(9)
C(4D)	11 526(13)	1 698(9)	8 913(9)
C(5D)	11 779(13)	2 042(9)	8 219(9)
C(6D)	10 904(13)	2 276(9)	7 717(9)



(1) [Co(salphen)]
(2) [Co(salen)]
(3) [Co{3,3′-(MeO)$_2$-salen}]
(4) [Co(α,α′-Et$_2$-salen)]
(5) [{Co(salphen)}$_2$S$_4$(thf)$_2$]
(6) [{Co(salphen)}$_2$S$_4$(py)$_2$]
(7) [{Co(salen)}$_2$S$_4$(thf)]
(8) [{Co(salen)}$_2$S$_4$(py)$_2$]
(9) [{Co[3,3′-(MeO)$_2$-salen]}$_2$S$_4$]
(10) [{Co(α,α′-Et$_2$-salen)}$_2$S$_4$(thf)]

Scheme 1.

Table 3. Fractional atomic co-ordinates (× 10^4) for $[\{Co(salphen)\}_2Na(thf)_2]BPh_4$, **(12)**

Atom	*X/a*	*Y/b*	*Z/c*
Co	2 133(2)	673(1)	1 979(1)
O(1)	1 878(6)	755(6)	2 851(6)
O(2)	2 972(6)	632(5)	2 314(6)
N(1)	1 293(8)	732(6)	1 646(8)
N(2)	2 398(9)	619(7)	1 113(8)
Co′	1 765(1)	1 853(1)	2 474(2)
O(1′)	2 085(6)	1 825(5)	3 339(6)
O(2′)	2 617(6)	1 726(5)	2 242(7)
N(1′)	888(8)	1 929(6)	2 731(8)
N(2′)	1 435(8)	1 881(6)	1 614(8)
Na	2 857(4)	1 212(3)	3 168(4)
O(1A)	3 146(11)	772(9)	4 109(7)
O(1B)	3 813(8)	1 642(10)	3 398(11)
C(1)	1 266(6)	776(6)	3 088(7)
C(2)	1 201(6)	795(6)	3 775(7)
C(3)	574(6)	816(6)	4 061(7)
C(4)	12(6)	817(6)	3 661(7)
C(5)	77(6)	798(6)	2 974(7)
C(6)	704(6)	777(6)	2 688(7)
C(7)	732(12)	787(8)	1 962(10)
C(8)	1 259(8)	759(6)	943(5)
C(9)	708(8)	853(6)	552(5)
C(10)	768(8)	866(6)	−136(5)
C(11)	1 380(8)	786(6)	−432(5)
C(12)	1 932(8)	692(6)	−40(5)
C(13)	1 872(8)	679(6)	647(5)
C(14)	2 961(11)	526(7)	893(9)
C(15)	3 556(7)	460(6)	1 307(8)
C(16)	4 157(7)	366(6)	997(8)
C(17)	4 733(7)	328(6)	1 372(8)
C(18)	4 708(7)	382(6)	2 058(8)
C(19)	4 107(7)	475(6)	2 368(8)
C(20)	3 530(7)	514(6)	1 992(8)
C(1′)	1 740(9)	1 891(6)	3 891(7)
C(2′)	2 104(9)	1 903(6)	4 477(7)
C(3′)	1 782(9)	1 968(6)	5 081(7)
C(4′)	1 096(9)	2 020(6)	5 097(7)
C(5′)	733(9)	2 009(6)	4 511(7)
C(6′)	1 055(9)	1 944(6)	3 907(7)
C(7′)	639(11)	1 978(8)	3 304(12)
C(8′)	450(8)	1 916(7)	2 197(7)
C(9′)	−236(8)	1 961(7)	2 228(7)
C(10′)	−606(8)	1 985(7)	1 646(7)
C(11′)	−290(8)	1 964(7)	1 033(7)
C(12′)	396(8)	1 919(7)	1 002(7)
C(13′)	766(8)	1 894(7)	1 584(7)
C(14′)	1 785(12)	1 860(9)	1 104(11)
C(15′)	2 495(6)	1 802(6)	1 078(9)
C(16′)	2 784(6)	1 794(6)	451(9)
C(17′)	3 460(6)	1 712(6)	386(9)
C(18′)	3 848(6)	1 638(6)	947(9)
C(19′)	3 559(6)	1 646(6)	1 574(9)
C(20′)	2 882(6)	1 728(6)	1 639(9)
B	2 500(0)	0(0)	7 473(18)
C(31)	2 899(7)	346(5)	8 002(6)
C(32)	2 698(7)	795(5)	8 124(6)
C(33)	3 025(7)	1 058(5)	8 599(6)
C(34)	3 553(7)	871(5)	8 952(6)
C(35)	3 754(7)	422(5)	8 830(6)
C(36)	3 427(7)	159(5)	8 355(6)
C(41)	1 987(7)	267(5)	6 978(6)
C(42)	1 344(7)	113(5)	6 860(6)
C(43)	944(7)	339(5)	6 403(6)
C(44)	1 187(7)	720(5)	6 063(6)
C(45)	1 829(7)	874(5)	6 181(6)
C(46)	2 229(7)	647(5)	6 638(6)
B′	2 183(16)	2 500(0)	7 500(0)
C(31′)	2 690(6)	2 275(5)	6 928(6)
C(32′)	3 010(6)	1 866(5)	7 082(6)
C(33′)	3 453(6)	1 672(5)	6 632(6)
C(34′)	3 575(6)	1 888(5)	6 028(6)
C(35′)	3 254(6)	2 298(5)	5 874(6)
C(36′)	2 812(6)	2 491(5)	6 324(6)
C(41′)	1 678(6)	2 105(5)	7 809(7)
C(42′)	1 343(6)	2 201(5)	8 396(7)
C(43′)	861(6)	1 899(5)	8 629(7)
C(44′)	715(6)	1 502(5)	8 276(7)
C(45′)	1 051(6)	1 405(5)	7 689(7)
C(46′)	1 532(6)	1 707(5)	7 456(7)
C(2A)	3 148(23)	941(19)	4 728(27)
C(3A)	3 416(28)	564(22)	5 164(24)
C(4A)	3 726(28)	297(22)	4 762(34)
C(5A)	3 311(33)	316(25)	4 190(29)
C(2B)	4 494(25)	1 473(18)	3 397(20)
C(3B)	4 820(25)	1 880(23)	3 398(24)
C(4B)	4 432(31)	2 248(21)	3 685(25)
C(5B)	3 760(20)	2 083(18)	3 429(20)

Results and Discussion

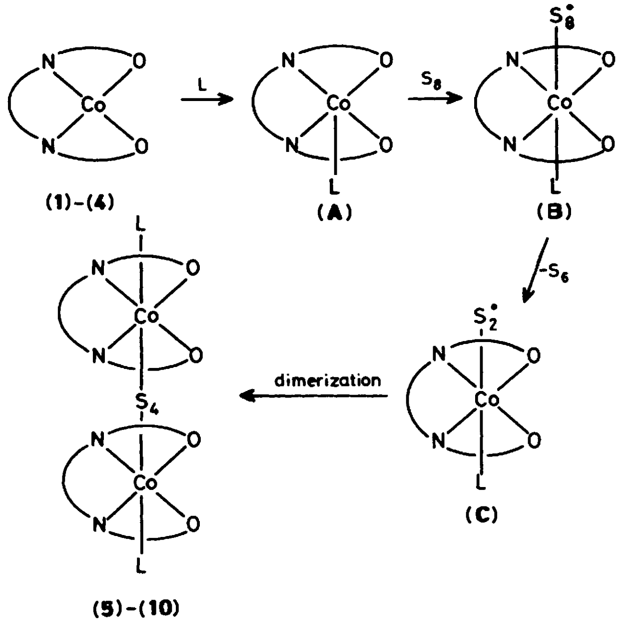
Cobalt(II)–Schiff-base complexes (**1**)—(**4**) containing the ligands listed in Scheme 1 reacted with elemental sulphur in the presence of a co-ordinating solvent, namely thf or py, which supplies a fifth donor atom around cobalt(II). The complexes formed are μ-tetrasulphido derivatives of cobalt(III).

Complexes (**5**)—(**10**) have been obtained as diamagnetic crystalline solids, having low solubility in many solvents. The 1:2 cobalt/sulphur ratio in the complexes (**5**)—(**10**) is independent of the Co/S ratio used in the reaction and of the nature of the quadridentate ligand and the axial solvent.

The requirement for a co-ordinating solvent is based on the tendency of cobalt to form a 17-electron free-radical type configuration.[7] Sulphur–sulphur bonds are known to be susceptible to free-radical attack.[6] A plausible pathway leading to the formation of complexes (**5**)—(**10**) is shown in Scheme 2.

For those complexes which do not contain co-ordinating solvent molecules, the axial position around cobalt can be filled by an oxygen from an adjacent molecule, in a fashion which is known in metal–Schiff-base chemistry.[23] The structure we propose for complexes (**5**)—(**10**) contains two cobalt(III) ions bridged by a tetrasulphido ligand, S_4^{2-}, though we cannot specify any structure or bonding mode of the S_4^{2-} unit. Although we were not able to grow crystals appropriate for an *X*-ray analysis, the proposed structure is well supported by analytical data, the diamagnetism of the compounds, similar results obtained in the reaction of cobalt–oxime derivatives with elemental sulphur (see later), and by the structure of a related μ-disulphido(2−)-dicobalt(III) complex (see later). The very low solubility of complexes (**5**)—(**9**) prevents n.m.r. measurements, while the i.r. spectra do not have distinctive features which can be useful for interpreting the structure of such compounds.

We have assumed that the formation of the S_2^- fragment as the most stable radical occurs at sulphur,[6] and that the reaction leading to it is much faster than that of the starting free radical with S_2^- to form a binuclear μ-disulphido(2−) complex, or that some instability can be attributed to the CoS_2Co unit (see later). The reactions of $[Co(CN)_5]^{3-}$ [refs. 7—11(*a*)] and $[Co(Hdmg)_2(py)R]$[24] (Hdmg = dimethylglyoximate, R = alkyl or aryl) with elemental sulphur have much in common with those reported in Scheme 2, namely the generation of S_2^- species and their dimerization to a tetrasulphido fragment. Reactions of cobalt(II)-centred radicals with elemental sulphur are highly reminiscent of their reactions

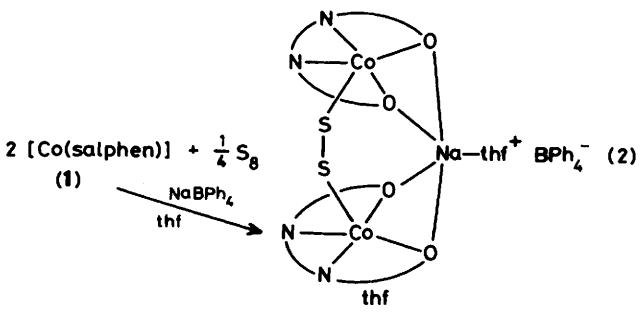


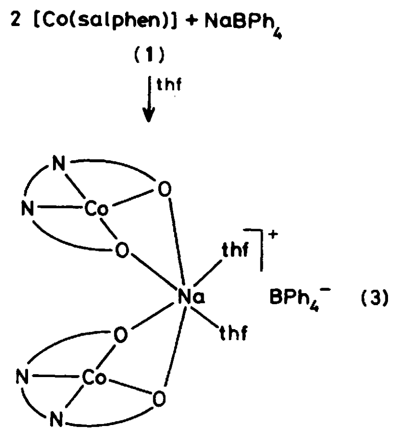
Scheme 2.

with molecular oxygen. In all cases the first step, based on isolated compounds or on their evolution, is the formation of a superoxo species, which unlike S_2^- does not dimerize. Probably the genesis and even the structural and electronic properties of the O_2 and S_2 derived species are related.

A significant change in the chemical reactivity of the cobalt in complexes (**1**)—(**4**) can be introduced by carrying out the reactions in the presence of cationic species. This is a consequence of the fact that the O—O bite in these complexes acts as a bidentate ligand towards alkali-metal and organic cations.[25-27] There are a number of consequences derived from the introduction of a cation into the complexes (**1**)—(**4**). Those which are relevant in the present context are: (*i*) the cobalt can undergo a change in redox properties, and (*ii*) the cation, acting as a template agent, can surround itself with more than one cobalt in close geometrical proximity.

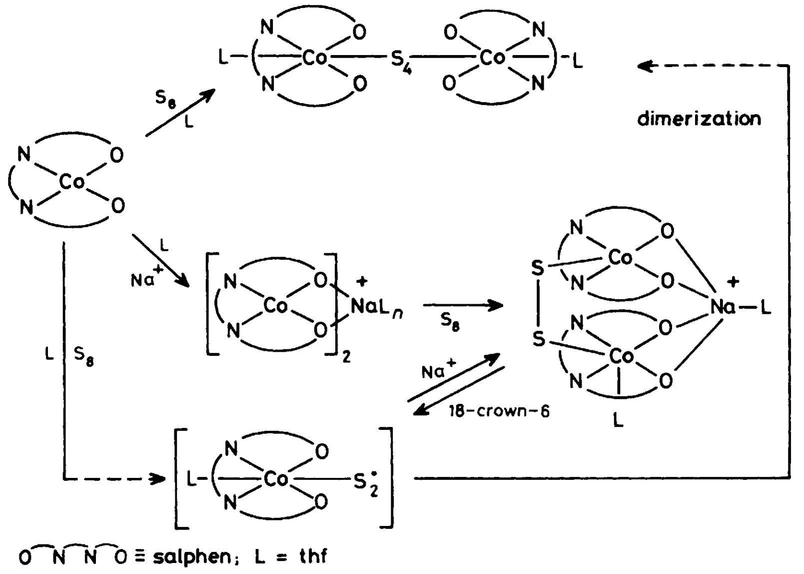
The complex [Co(salphen)] reacted with elemental sulphur in the presence of $NaBPh_4$ to give (**11**) [see equation (2)].





Complex (**11**) is the only isolable product from reaction (2), and it is a diamagnetic compound of very high stability. The structure of (**11**), determined by an *X*-ray study, will be discussed later. The sodium cation dramatically influences the reaction of (**1**) with S_8. Preliminary to understanding the genesis of (**11**) it should be mentioned that (**1**) binds $NaBPh_4$ in thf solution to form (**12**), which was isolated in the solid state (see later) [see equation (3)]. The controlling action of Na^+ in reaction (3) can be viewed in two different ways as shown in Scheme 3.

The complex [Co(salphen)] in thf containing $NaBPh_4$ binds



Scheme 3.

Na^+ to form complex (**12**), which is probably the species which reacts with elemental sulphur to give complex (**11**). Another plausible role for Na^+ could be that of causing a rearrangement of a sulphur–cobalt species. Doubtless, the way in which Na^+ drives the reaction in Scheme 1 to result in reaction (2) depends on its ability to force together two [Co(salphen)] units, to make a cavity of the appropriate size for the S_2 unit. That the ability of the cation to control cavity size is a fundamental parameter of this reaction was demonstrated indirectly by the results obtained upon carrying out the reaction (1) in the presence of lithium, potassium, and guanidinium cations. It should be pointed out that potassium and guanidinium cations are complexed by M(salen) type ligands to form *e.g.* $[\{\mathrm{Ni(salen)}\}_3\mathrm{K}]\mathrm{BPh_4}$, (**13**),[25c] and $[\{\mathrm{Ni(salen)}\}_3\mathrm{C(NH_2)_3}]\mathrm{BPh_4}$, (**14**).[26b]

It should also be noted that the two structures (**11**) and (**12**) are quite similar, as is demonstrated by a comparison of structural parameters. Attention is also drawn to the cavity existing between the two [Co(salphen)] units, as a consequence of the Na^+ binding [see the description of the structures of (**11**) and (**12**) later in this paper].

The reaction of [Co(salphen)] with S_8 in the presence of Li^+, K^+, and $[C(NH_2)_3]^+$ cations gave the results reported in reactions (4)—(6). Compounds (**15**)—(**17**) have been obtained

$$2[\mathrm{Co(salphen)}] + \tfrac{1}{2}S_8 \xrightarrow[\text{thf}]{\text{LiBPh}_4} \underset{\textbf{(15)}}{[\{\mathrm{Co(salphen)S_2(thf)}\}_2\mathrm{Li}]\mathrm{BPh_4}} \quad (4)$$

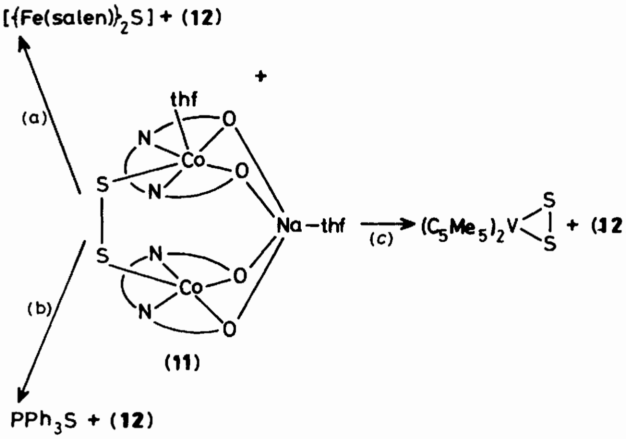
$$3[\mathrm{Co(salphen)}] + \tfrac{6}{8}S_8 \xrightarrow[\text{thf}]{\text{KBPh}_4} \underset{\textbf{(16)}}{[\{\mathrm{Co(salphen)S_2(thf)}\}_3\mathrm{K}]\mathrm{BPh_4}} \quad (5)$$

$$3[\mathrm{Co(salphen)}] + \tfrac{6}{8}S_8 \xrightarrow[\text{thf}]{[\mathrm{C(NH_2)_3}]\mathrm{BPh_4}} \underset{\textbf{(17)}}{[\{\mathrm{Co(salphen)S_2(thf)}\}_3\mathrm{C(NH_2)_3}]\mathrm{BPh_4}} \quad (6)$$

in crystalline forms, though not suitable for an *X*-ray analysis. The Co/S_2 molar ratio and the diamagnetism of all three compounds seem to suggest that the basic unit in these polysulphido derivatives is the CoS_4Co moiety found in complexes (**5**)—(**10**). This leads to the conclusion that these cations do not substantially affect reaction (1), except in the area of binding of the oxygen atoms of a $[\{\mathrm{Co(salphen)}\}_2S_4]$ unit. This lack of influence on reaction (1) may be associated with the kind of arrangement that the cation imposes on the [Co(salphen)] ligands. This arrangement, *i.e.* in complexes (**13**) and (**14**), does not provide any metal–metal proximity or cavity by which a S_n fragment can be preferentially stabilized. The S_4 units bridge, very probably, two metals belonging to two different $[\{\mathrm{Co(salphen)}\}_2\mathrm{Li}]^+$, $[\{\mathrm{Co(salphen)}\}_3\mathrm{K}]^+$, or $[\{\mathrm{Co(salphen)}\}_3\mathrm{C(NH_2)_3}]^+$ cations in complexes (**15**)—(**17**). It has to be mentioned that Na^+ not only provides a special pathway for CoS_2Co formation, but even that the stability of this moiety depends on the presence of a Na^+ cation in (**11**). An attempt to remove Na^+ by treating complex (**11**) with 18-crown-6 resulted in decomposition, as shown in reaction (7).

$$\underset{\textbf{(11)}}{[\{\mathrm{Co(salphen)}\}_2S_2\mathrm{Na(thf)_2}]^+} \xrightarrow[-\mathrm{Na}^+]{\text{18-crown-6}} \underset{\textbf{(5)}}{[\{\mathrm{Co(salphen)}\}_2S_4\mathrm{(thf)_2}]} + \underset{\textbf{(1)}}{[\mathrm{Co(salphen)}]} \quad (7)$$

This result may suggest that the removal of Na^+ from (**11**) frees the $[\mathrm{Co(salphen)}S_2]^{\bullet}$ radical which, as in Scheme 3, dimerizes to (**5**).[24] The stability of the binuclear structure shown in (**11**) is associated much more with the presence of Na^+ than with the presence of the bridging S_2 unit. The $S_2{}^{2-}$ ligand can be removed from (**11**) leaving the structure intact in the form of complex (**12**). To this end, some desulphurization reactions have been carried out on (**11**) as represented in Scheme 4. Transfer of a single sulphur atom occurs in reactions (a) and (b), while in reaction (c) the S_2 unit is transferred to $[V(\eta\text{-}C_5Me_5)_2]$ to form $[\{V(\eta\text{-}C_5Me_5)_2\}S_2]$.[28,29]



Scheme 4. (a), [Fe(salen)]; (b), PPh_3; (c), $[V(\eta\text{-}C_5Me_5)_2]$

Structure of Complex (**11**).—The two Co(salphen) units are bridged by S_2 bonding the two cobalt atoms, while the sodium cation is anchored to the four oxygens of these two units (Figure 1). While the two Co(salphen) molecules are nearly parallel (Figure 2) in (**12**), they are in a bent arrangement to make a cavity for the S_2 bridge in (**11**).

The dihedral angle between the mean planes through the Co(salphen) molecules is 50.3(1)°. The torsional angle around the S–S bond is 108.0(4)° and the S–S distance is 1.962(9) Å with some significant double-bond character.[9,30] The overall geometry of the dimer is very close to that found in the peroxo derivative $[\mathrm{(dmf)(salen)CoO_2Co(salen)(dmf)}]$ (dmf = *NN*-dimethylformamide),[31] except for the orientation of the two cobalt–Schiff base moieties which, in (**11**), is mainly imposed by Na^+. The geometry of the S_2 bridge is largely imposed by the mutual arrangement of the two Co(salphen) units bonded to the same sodium cation. The Co–S distances [Co–S 2.231(7), Co′–S′ 2.249(7) Å] are not affected by the difference in the co-ordination geometry around cobalt.[32] Cobalt is 0.130(4) Å out of the O(1), N(1), N(2), O(2) plane towards sulphur. The direction of the Co–S bond is tilted by 6.0(4)° with respect to the normal of this plane. Co-ordination around Co′ is more planar, Co′ being only 0.054(3) Å out of the donor atom plane towards S′. The Co′–S′ and Co′–O(1B) bonds form angles of 4.8(3) and 2.4(6)° with the normals to that plane.

The co-ordination geometry is only slightly affected by the presence of the Na and S_2 bridges.[24] Bond distances and angles involving the cobalt atoms agree well with those observed in [Co(salphen)][33] and in complex (**12**), the only difference being the O(1)–Co–N(2) angle [169.6(7)°] which shows a more significant departure from 180°. The unprimed salphen moiety is nearly planar, the maximum displacement [0.142(14) Å] being observed for O(2). The cobalt atom is 0.174(3) Å out of this plane on the same side as O(2), S, and Na. The primed salphen molecule is folded, the planar group of N′, O′, C(1′) $\cdots$ C(7′) atoms being folded down by 14.7(3)° with respect to the mean plane running through the rest of the molecule in a direction opposite to the S_2 bridge. The O(2′) atom is 0.127(14) Å out of this last plane towards sodium; all the other deviations are less than 0.096(15) Å. The distortions

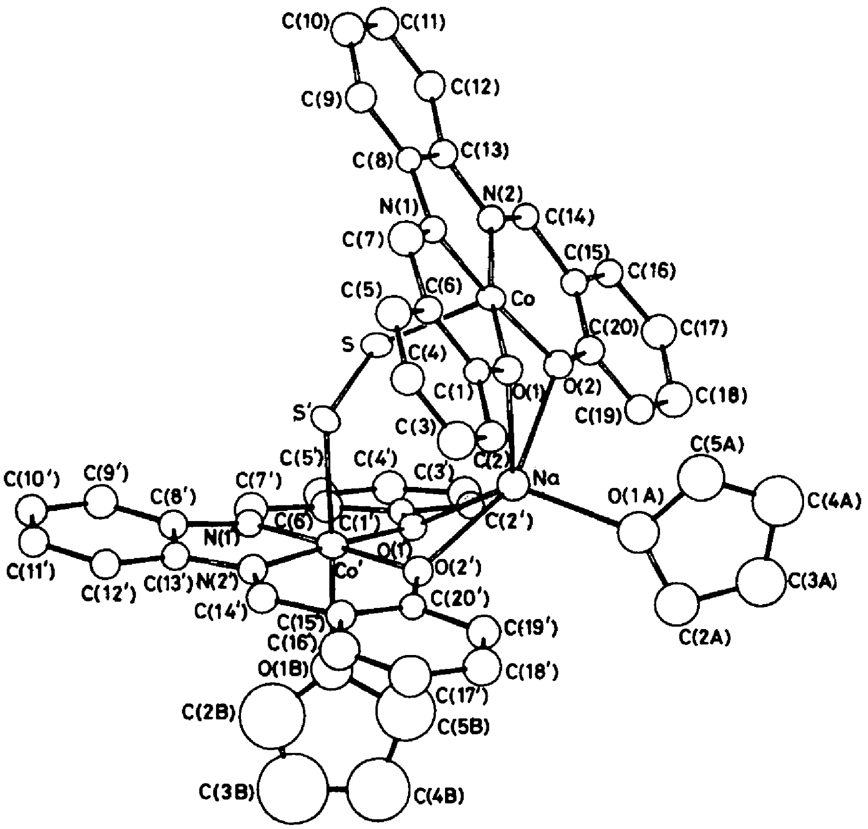


Figure 1. An ORTEP drawing for the $[\{Co(salphen)\}_2(\mu\text{-}S_2)Na(thf)_2]^+$ cation of complex (11), showing 30% probability ellipsoids

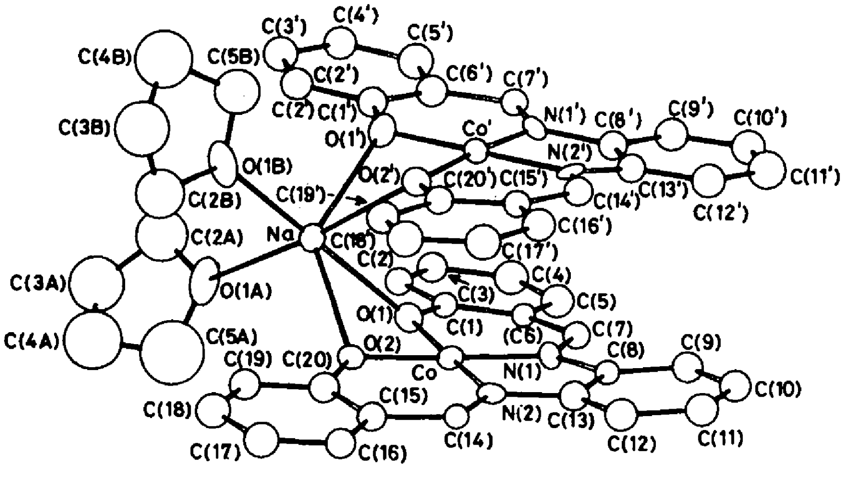


Figure 2. An ORTEP drawing for the cation $[\{Co(salphen)\}_2Na(thf)_2]^+$ of complex (12), showing 30% probability ellipsoids

observed appear to be a consequence of the binding of sodium and of steric hindrance with the sulphur bridge, since the shortest intramolecular contacts between the two Co(salphen) units involve the sulphur atoms: S $\cdots$ O(1') 3.23(2), S' $\cdots$ O(1) 3.32(2) Å.

The thf molecules are affected by high thermal motion and this could be the reason why the O(1B)—C(5B) molecule does not deviate significantly from planarity. The O(1A)—C(5A) molecule shows an envelope conformation with O(1A) significantly out of the plane through the other four atoms [0.37(2) Å].

Structure of Complex (12).—The structure consists of discrete cations, $[\{Co(salphen)\}_2Na(thf)_2]^+$, and BPh_4^- anions separated by van der Waals contacts. The cation has a local C_2 symmetry with two Co(salphen) units anchored to a sodium through the four oxygens (Figure 2). Co-ordination around sodium is completed by the oxygen atoms from two thf molecules. The geometry of each Co(salphen) unit (Table 4) agrees well with that observed in [Co(salphen)].[33] The two Co(salphen) units are approximately planar and nearly parallel, the dihedral angle between the mean planes through them being 4.0(1)°. The distance between the two planes is 2.92(1) Å. They

Table 4. Selected bond distances (Å) and angles (°) for complexes (**11**) and (**12**)

	(**11**)	(**12**)		(**11**)	(**12**)
Co–O(1)	1.88(1)	1.85(1)	Co′–O(1′)	1.88(1)	1.86(1)
Co–O(2)	1.88(1)	1.83(1)	Co′–O(2′)	1.88(1)	1.82(1)
Co–N(1)	1.87(2)	1.84(2)	Co′–N(1′)	1.88(2)	1.86(1)
Co–N(2)	1.86(2)	1.84(2)	Co′–N(2′)	1.85(2)	1.86(1)
Co–S	2.231(7)		Co′–S′	2.249(7)	
			Co′–O(1B)	2.22(2)	
Na–O(1)	2.41(2)	2.47(2)	Na–O(1′)	2.38(2)	2.40(2)
Na–O(2)	2.36(2)	2.43(2)	Na–O(2′)	2.34(2)	2.45(2)
Na–O(1A)	2.30(2)	2.37(2)	Na–O(1B)	—	2.35(2)
Co–S–S′	112.2(4)		Co′–S′–S	112.4(4)	

do not overlap, but are shifted and rotated with respect to each other resulting in a Co ··· Co′ distance of 3.664(4) Å, and in the following intramolecular distances shorter than 3.40 Å: Co–O(2′) 3.27(1), Co′–O(1) 3.30(2), O(1) ··· O(1′) 3.30(2), O(2) ··· O(2′) 3.28(2), N(1) ··· N(2′) 3.37(2) Å.

The Co(salphen) units show a conformation slightly distorted towards an umbrella shape. The phenyl rings are folded with respect to the mean planes through the chelation rings by 6.4(4), 6.3(4), and 4.0(4)° for the rings C(1)—C(6), C(8)—C(13), and C(15)—C(20) respectively, and by 3.8(5), 1.7(5), and 6.9(5)° for the corresponding primed rings, apparently in order to release steric interactions. The oxygen atoms are displaced out of the chelation ring planes towards sodium. The co-ordination geometry, however, appears not to be significantly affected, the O–Co–O angles being practically unchanged from those of [Co(salphen)] {84.8(6) (mean) *vs.* 85.1(4)° (mean) in [Co(salphen)]};[33] the cobalt atom in both units has nearly planar geometry with deviations of the metal and its donor atoms from their mean plane not exceeding 0.044(20) and 0.086(17) Å for Co and Co′ respectively. The Na–O distances fall in the usual range. The two thf molecules, which are affected by high thermal motion, have an envelope conformation, the C(4A) and C(4B) atoms being out of the respective planes through the other four atoms by 0.55(6) and 0.52(5) Å respectively. These two planes are nearly orthogonal, the dihedral angle being 81.2(2)°.

In the asymmetric unit there are two halves of BPh_4^- anions with the boron atoms lying on two-fold axes.

References

1 M. Draganjac and T. B. Rauchfuss, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 742; R. Steudel and R. Strauss, *J. Chem. Soc., Dalton Trans.*, 1984, 1775; C. M. Bolinger, T. B. Rauchfuss, and A. L. Rheingold, *Organometallics*, 1982, **1**, 1551; *J. Am. Chem. Soc.*, 1983, **105**, 6321; R. Weberg, R. C. Haltiwanger, and M. Rakowski-Dubois, *Organometallics*, 1985, **4**, 1315; F. Bottomley, G. O. Egharevba, and P. S. White, *J. Am. Chem. Soc.*, 1985, **107**, 4353.

2 H. Varenkamp, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 322.

3 A. Muller, E. Diemann, R. Jostes, and H. Bogge, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 934.

4 A. Müller, W. Jaegermann, and J. H. Enemark, *Coord. Chem. Rev.*, 1982, **46**, 245.

5 D. Coucouvanis, *Acc. Chem. Res.*, 1981, **14**, 201; R. H. Holm, *ibid.*, 1977, **20**, 427; R. E. Palermo, R. Singh, J. K. Bashkin, and R. H. Holm, *J. Am. Chem. Soc.* 1984, **106**, 2600; J. A. Kovacs, J. K. Bashkin, and R. H. Holm, *ibid.*, 1985, **107**, 1784 and refs. therein.

6 J. L. Rice, 'The Sulfur-Sulfur Bond,' in 'Sulfur in Organic and Inorganic Chemistry,' ed. A. Senning, Marcel Dekker, New York, 1971, vol. 1, ch. 6; J. C. Rabinovitz, *Adv. Chem. Ser.*, 1971, **100**, 322.

7 J. Halpern, *Adv. Chem. Ser.*, 1968, **70**, 1.

8 R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, 1979, **79**, 139; G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, 1976, **19**, 1; J. P. Collman, *Acc. Chem. Res.*, 1977, **10**, 265; S. Fallab and P. R. Mitchell, 'Advances in Inorganic and Bioinorganic Mechanisms,' Academic Press, New York, 1984, vol. 3, pp. 311–377; L. Vaska, *Acc. Chem. Res.*, 1976, **9**, 175.

9 A. P. Ginsberg and W. E. Lindsell, *Chem. Commun.*, 1971, 232; W. D. Bonds, jun., and J. A. Ibers, *J. Am. Chem. Soc.*, 1972, **94**, 3413; T. E. Nappier, jun., and D. W. Meek, *ibid.*, p. 306; T. E. Nappier, jun., D. W. Meek, R. M. Kirchner, and J. A. Ibers, *ibid.*, 1973, **95**, 4194; D. H. Farrar, K. R. Grundy, N. C. Payne, W. R. Roper, and A. Walker, *ibid.*, 1979, **101**, 6577; G. R. Clark, D. R. Russell, W. R. Roper, and A. Walker, *J. Organomet. Chem.*, 1977, **136**, Cl; J. T. Mague and E. J. Davies, *Inorg. Chem.*, 1977, **16**, 131.

10 R. S. Drago, *Coord. Chem. Rev.*, 1980, **32**, 97.

11 (*a*) H. Siebert and S. Thym, *Z. Anorg. Allg. Chem.*, 1973, **399**, 107; (*b*) G. T. Kubas, T. G. Spiro, and A. Terzis, *J. Am. Chem. Soc.*, 1973, **95**, 273; A. Terzis and R. Rivest, *Inorg. Chem.*, 1973, **12**, 2132; C. R. Brulet, S. S. Isied, and H. Taube, *J. Am. Chem. Soc.*, 1973, **95**, 4758; R. C. Elder and M. Trkula, *Inorg. Chem.*, 1977, **16**, 1048; C. G. Kuehn and S. S. Isied, *Prog. Inorg. Chem.*, 1979, **27**, 153.

12 S. Gambarotta, M. L. Fiallo, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1982, 503.

13 C. Floriani and F. Calderazzo, *J. Chem. Soc. A*, 1969, 946.

14 S. Gambarotta, F. Arena, C. Floriani, and P. F. Zanazzi, *J. Am. Chem. Soc.*, 1982, **104**, 5082.

15 F. Calderazzo, C. Floriani, R. Henzi, and F. L'Eplattenier, *J. Chem. Soc. A*, 1969, 1378.

16 S. Gambarotta, C. Floriani, A. Chiesi-Villa, and C. Guastini, *Inorg. Chem.*, 1984, **23**, 1739.

17 C. Floriani, A. Chiesi-Villa, and C. Guastini, unpublished work.

18 G. M. Sheldrick, SHELX 76, A system of crystallographic computer programs, University of Cambridge, 1976.

19 S. L. Lawton and R. A. Jacobson, TRACER, A cell reduction program, Ames Laboratory, Iowa State University of Science and Technology, 1965.

20 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580.

21 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, (*a*) p. 99; (*b*) p. 149.

22 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

23 M. Calligaris, G. Nardin, and L. Randaccio, *Coord. Chem. Rev.*, 1972, **7**, 385; M. D. Hobday and T. D. Smith, *ibid.*, 1972–1973, **9**, 311.

24 C. Giannotti and G. Merle, *J. Organomet. Chem.*, 1976, **113**, 45; C. Giannotti, C. Fontaine, B. Septe, and D. Doue, *ibid.*, 1972, **39**, C74.

25 (*a*) S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1805; H. Milburn, M. R. Truter, and B. L. Vickery, *J. Chem. Soc., Dalton Trans.*, 1974, 841; L. G. Armstrong, H. C. Lip, L. F. Lindoy, M. McPartlin, and P. A. Tasker, *ibid.*, 1977, 1771; M. Pasquali, F. Marchetti, C. Floriani, and M. Cesari, *Inorg. Chem.*, 1980, **19**, 1198; (*b*) L. Randaccio, *Gazz. Chim. Ital.*, 1974, **104**, 991; D. E. Fenton, N. Bresciani-Pahor, M. Calligaris, G. Nardin, and L. Randaccio, *J. Chem. Soc., Chem. Commun.*, 1979, 39; (*c*) N. Bresciani-Pahor, M. Calligaris, P. Delise, G. Nardin, L. Randaccio, E. Zotti, G. Fachinetti, and C. Floriani, *J. Chem. Soc., Dalton Trans.*, 1976, 2310.

26 (*a*) E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc. A*, 1970, 396; (*b*) A. Giacomelli, C. Floriani, and G. Perego, *J. Chem. Soc., Chem. Commun.*, 1982, 650.

27 A. Giacomelli, T. Rotunno, and L. Senatore, *Inorg. Chem.*, 1985, **24**, 1303.

28 S. Gambarotta, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1983, 184.

29 S. A. Koch and V. Chebolu, *Organometallics*, 1983, **2**, 350.

30 M. G. B. Drew, D. M. Williams, and D. A. Rice, *Inorg. Chim. Acta*, 1984, **89**, L19 and refs. therein; A. Muller and W. Jaegermann, *Inorg. Chem.*, 1979, **18**, 2631; R. Mercier, J. Douglade, J. Amaudrut, J. Sala-Pala, and J. Guerchais, *Acta Crystallogr., Sect. B*, 1980, **36**, 2986.

31 M. Calligaris, G. Nardin, L. Randaccio, and A. Ripamonti, *J. Chem. Soc. A*, 1970, 1069.

32 V. A. Uchtman and L. F. Dahl, *J. Am. Chem. Soc.*, 1969, **91**, 3756.

33 N. Bresciani-Pahor, M. Calligaris, P. Delise, G. Dodic, G. Nardin, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 1976, 2478.

Received 28th May 1986; *Paper* 6/1054