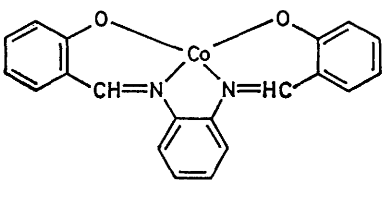
Alkali Metal Cations controlling the Reactivity of Cobalt(II) Schiff Base Complexes: Synthesis of a μ-Persulphido-ligand from S_8 reacting with a Cobalt(II) Oxygen Carrier Compound

S. Gambarotta,[a] M. L. Fiallo,[a] C. Floriani,*[a] A. Chiesi-Villa,[b] and C. Guastini[b]

[a] *Istituto di Chimica Generale, Università di Pisa, 56100 Pisa, Italy*
[b] *Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica CNR, Università di Parma, 43100 Parma, Italy*

Elemental sulphur reacted with *N,N′-o*-phenylenebis(salicylideneaminato)cobalt(II), [Co(salophen)] in tetrahydrofuran or pyridine solution to produce tetrasulphido-cobalt(III) complexes, [(L)(salophen)Co–S_4–Co(salophen)(L)] [L = tetrahydrofuran (thf), pyridine (py)]; when the same reaction was carried out in the presence of a sodium cation bonded by [Co(salophen)], the isolation of a μ-persulphido-dicobalt(III) complex, {[(thf)(salophen)Co–S_2–Co(salophen)][Na(thf)]}[BPh_4] was achieved [S–S, 1.962(9) Å].

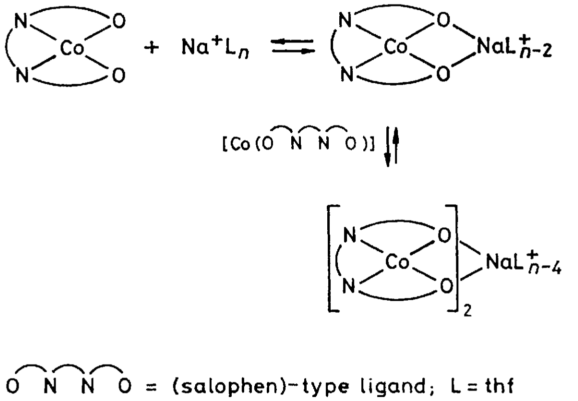
Persulphido[1] (-S-_2) and supersulphido[2] ($\text{-}S_2^{-}\text{-}$) units can be generated from S_8 by free radical-like complexes capable of binding O_2 either in the superoxo- or in the peroxo-form,[2] the S–S bond being highly susceptible to free radical attack.[3] In *N,N′-o*-phenylenebis(salicylideneaminato) cobalt(II), [Co(salophen)] (**1**) a square planar cobalt(II) becomes a free radical-like five-co-ordinate cobalt(II), having seventeen electrons, on the action of a co-ordinating solvent like tetrahydrofuran (thf) or pyridine (py).[4] The present report deals with the reactivity



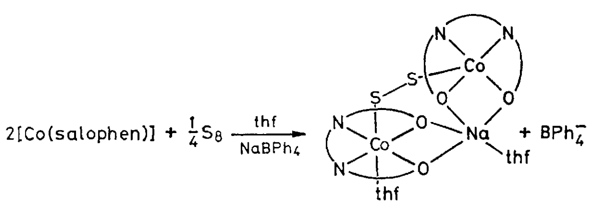
(**1**)

of (1) with elemental sulphur, and with the influence which alkali metal cations can have on this reactivity.

Alkali metal cations act in the appropriate solvents as complex carriers, binding the two oxygens of a metal tetradentate Schiff-base complex,[5] equation (1), and thus affect the redox potential of the transition metal. They can also act as template agents in controlling the molecular complexity and the mutual position of transition metal centres.[5,6] This may be important when more than one centre is interacting with a given substrate, as shown below.



(1)



(2)

(2)

[Co(salophen)] dissolves in thf on addition of $NaBPh_4$. The resulting thf solution reacts with elemental sulphur giving maroon crystals of {[(thf)(salophen)Co–S_2–Co(salophen)] [Na(thf)]}[BPh_4], (2), equation (2), the reactive species being a [Co(salophen)]–Na^+ adduct, equation (1), as proven by the different results obtained in its absence (*vide infra*). The nature of (2), which is diamagnetic and analysed correctly for the proposed formula, was completely clarified by an *X*-ray analysis.†

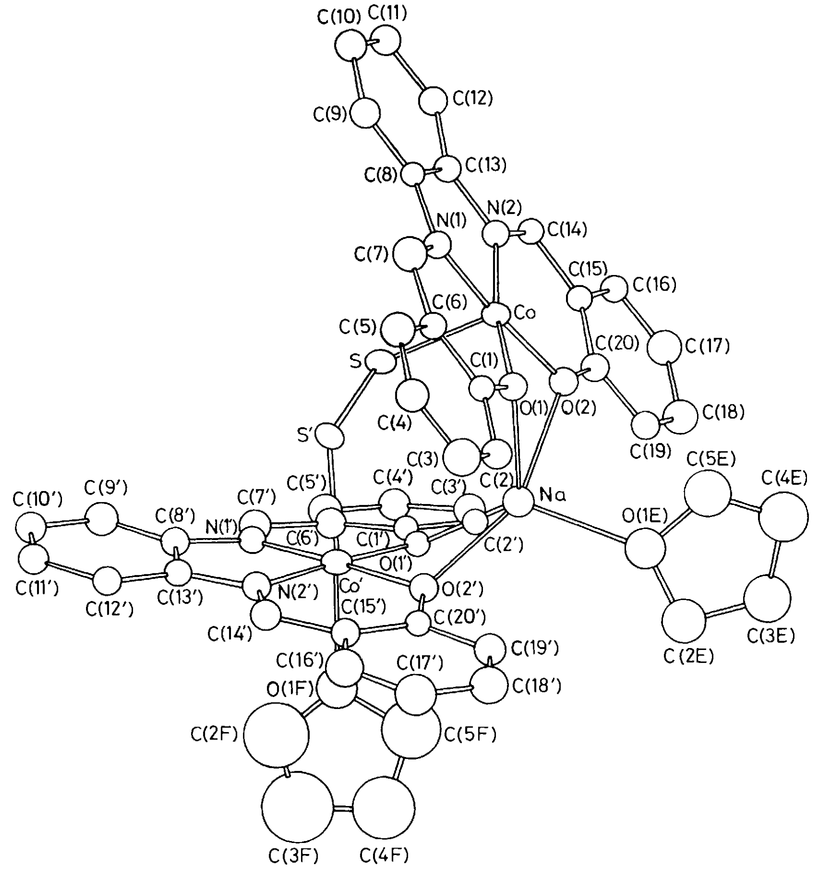


Figure 1. An ORTEP diagram of the cation present in complex (2), {[(thf)(salophen)Co–S_2–Co(salophen)][Na(thf)]}$^+$. Bond distances: S–S′, 1.962(9); Co–S, 2.231(7); Co′–S′, 2.249(7); Co–O(1), 1.875(15); Co–O(2), 1.876(15); Co–N(1), 1.868(18); Co–N(2), 1.859(18); Co′–O(1′), 1.878(14); Co′–O(2′), 1.881(14); Co′–N(1′), 1.877(17); Co′–N(2′), 1.850(18); Co′–O(1F), 2.223(21); Na–O(1), 2.412(18); Na–O(2), 2.363(17); Na–O(1′), 2.384(17); Na-O(2′), 2.337(16); Na–O(1E), 2.297(20) Å.

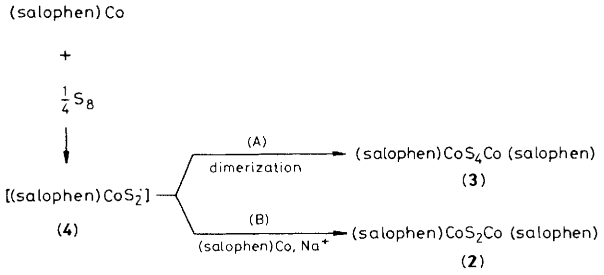
---

† *Crystal data:* $C_{72}H_{64}BCo_2N_4NaO_6S_2$, M = 1297.1, triclinic, $P\bar{1}$, a = 11.816(1), b = 15.549(2), c = 17.437(2) Å, α = 93.70(1), β = 93.90(1), γ = 94.86(1)°, U = 3176.8(6) Å^3, Z = 2, D_c = 1.356 g cm^{-3}, $F(000)$ = 1348 electrons, Mo-K_α radiation (λ = 0.71069 Å), μ(Mo-K_α) = 6.44 cm^{-1}. The structure was solved by conventional heavy atom methods (Patterson and Fourier) and refined by full-matrix blocked cascade least-squares. For 1479 unique observed structure amplitudes [$I > 2\sigma(I)$] collected at room temperature on a Siemens AED diffractometer in the range $5 < 2\theta < 44°$, the current R is 0.059. Owing to the small number of observed reflections, only the cobalt and sulphur atoms were allowed to vary anisotropically and all the Ph rings were treated as rigid groups having D_{6h} symmetry. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The cation present in complex **(2)** is shown in Figure 1. The two [Co(salophen)] units are bridged by the S_2 unit bonding the two cobalt atoms, while the sodium cation is anchored to the four oxygens from two [salophen] units. The torsional angle around the S–S bond is 108.10(4)° and the S–S bond distance is 1.962(9) Å with significant double bond character.[7] The geometry of the S_2 bridge is largely imposed by the mutual arrangement of the two [Co(salophen)] units bonding the same sodium cation; distorted square pyramidal co-ordination around sodium is completed by an oxygen atom from a thf molecule, and Na^+ bonding two [Co(salophen)] units generates an appropriate cavity for the S_2 unit. The Co–S bond distances [Co–S, 2.231(7); Co′–S′, 2.249(7) Å] are very similar despite the different co-ordination geometries around the cobalt atoms, *viz.* a square pyramid around Co with [salophen] nearly planar and cobalt 0.174(3) Å out of this plane towards sulphur, and an octahedron around Co′ using an oxygen from a thf molecule. The primed [salophen] moiety is folded by 13° with respect to the N(1′) . . . O(1′) line, probably as a consequence of steric hindrance with the sulphur bridge [O(1′) . . . S, 3.23(2) Å].

The persulphido-unit is closely related in its genesis and in its structural properties to the peroxo-ligand, in analogous complexes.[2,8] In dioxygen chemistry the superoxo-unit seems to be the precursor of the peroxo-unit;[2] similarly, a supersulphido-species could be formed *en route* to **(2)**. Indirect support for this hypothesis comes from the reaction between **(1)** and S_8 carried out in the absence of $NaBPh_4$ (which also emphasizes the special rôle played by the alkali metal cation in this and in related chemistry).

[Co(salophen)] is poorly soluble in thf and in py except when S_8 is added. The final solutions gave, on addition of Et_2O, microcrystalline black–maroon solids analysing as [(L)(salophen)Co–S_4–Co(salophen)(L)] (L = thf, py), **(3)**, which are diamagnetic. We previously reported a similar result using pyridine solution or suspension of [Co(salen)] or [Co(3MeOsalen)] (salen = salicylidenaminato) complexes[9] and an analogous S_4 unit was proposed to form *via* a free radical process involving a photochemically promoted insertion of elemental sulphur into a cobalt–carbon σ-bond.[10]



(3)

The final Co/S molar ratio in **(2)** and **(3)** is independent of the starting amount of elemental sulphur used. The genesis of [CoS_2Co] and [CoS_4Co] units may well involve the same supersulphido-precursor[10] as that formed by the attack of a free radical metal on the S–S bond of S_8 molecule,[3] equation (3). Pathway (A) is followed in the absence of Na^+, which forces the reaction to follow pathway (B). The sodium cation, being able to arrange around itself two [Co(salophen)] ligands with a well defined mutual arrangement, thus has a determining influence on the formation of complexes **(2)** *vs.* complexes **(3)**. Unfortunately we do not have any support so far for the existence of the intermediate **(4)**. The present results provide a new perspective in the use of cationic species in transition metal–Schiff base chemistry.

This work was supported by CNR (Rome).

Received, 5th February 1982; Com. 124

References

1 H. Siebert and S. Thym, *Z. Anorg. Allg. Chem.*, 1973, **399**, 107.

2 R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, 1979, **79**, 139 and references cited therein; C. Floriani and F. Calderazzo, *J. Chem. Soc. A*, 1969, 946.

3 J. L. Rice, 'Sulfur in Organic and Inorganic Chemistry,' ed. A. Senning, Marcel Dekker, N.Y., 1971, vol. 1, p. 953.

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

5 C. Floriani, F. Calderazzo, and L. Randaccio, *J. Chem. Soc., Chem. Commun.*, 1973, 384; 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; G. Fachinetti, C. Floriani, P. F. Zanazzi, and A. R. Zanzari, *Inorg. Chem.*, 1979, **18**, 3469; M. Pasquali, F. Marchetti, C. Floriani, and M. Cesari, *ibid.*, 1980, **19**, 1198.

6 A. Giacomelli and C. Floriani, in preparation.

7 W. D. Bonds and J. A. Ibers, *J. Am. Chem. Soc.*, 1972, **94**, 3413; A. P. Ginsberg and W. L. Lindsell, *Chem. Commun.*, 1971, 232 and references cited therein; P. J. Vergamini, R. R. Ryan, and G. J. Kubas, *J. Am. Chem. Soc.*, 1976, **98**, 1980; M. Herberhold, D. Reiner, B. Zimmer-Gesser, and U. Schubert, *Z. Naturforsch., Teil. B*, 1980, **35**, 1281; R. C. Elder and M. Trkula, *Inorg. Chem.*, 1977, **16**, 1048; W. Cligg, G. Christou, C. D. Garner, and G. M. Sheldrick, *Inorg. Chem.*, 1981, **20**, 1562; A. Müller, W. O. Nolte, and B. Krebs, *Angew. Chem., Int. Ed., Engl.*, 1978, **17**, 279.

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

9 C. Floriani and G. Fachinetti, *Gazz. Chim. Ital.*, 1973, **103**, 1317.

10 C. Giannotti, C. Fontaine, B. Septe, and D. Doue, *J. Organomet. Chem.*, 1972, **39**, C 74.