Factors Affecting the Addition of Sulphur Dioxide and Nitric Oxide to μ-Peroxo-dicobalt(III) Complexes and the Reactions with μ-Superoxo-complexes

By **Chen-Hwa Yang, David P. Keeton,** and **A. Geoffrey Sykes,*** Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT

The reactions of nine μ-peroxo-dicobalt(III) complexes with gaseous SO_2, liquid SO_2, and aqueous sulphite have been investigated. Whereas double-bridged complexes (*A*)—(*C*) having more exposed O_2-bridges give μ-sulphato-products under all conditions except aqueous solutions pH > *ca.* 6, single-bridged complexes (*D*)—(*H*) give significant reaction only after extensive treatment with liquid SO_2. Single-bridged μ-sulphato-complexes are believed to be formed, but these readily undergo bridge cleavage in aqueous solutions. The procedure previously reported for the preparation of the μ-sulphato-complex $[(NO_2)_2(NH_3)_3Co{\cdot}SO_4{\cdot}Co(NH_3)_3(NO_2)_2],2H_2O$ has been shown to give instead $[Co(NH_3)_3(NO_2)_2(H_2O)]_2SO_4$. Two μ-amido-μ-superoxo-complexes (*J*) and (*K*) do not react with SO_2 in the gas phase, but give the μ-amido-μ-sulphato-product with SO_2 in the liquid phase and in aqueous solution. Reactions of (*A*) and (*J*) with NO have also been investigated. In aqueous solutions complex (*J*) is first reduced to (*A*) which then gives the μ-amido-μ-nitrito-complex.

MONONUCLEAR diamagnetic oxygen complexes with an O_2-group bonded sideways to the metal are obtained by oxygenation of square-planar complexes of Ru, Rh, Ir, Pd, and Pt,[1] *e.g. trans*-$Ir(PPh_3)_2(CO)Cl$. Formation of such complexes with the activation of the oxygen provides a pathway for the catalytic oxidation of substrate molecules.[2,3] Thus with SO_2 as reactant, products containing chelated sulphate are obtained. Reactions with NO, N_2O_4, and CO have also been studied,[3] and with NO it has been found that *cis*-dinitro-complexes are obtained.

Processes involved in the activation of molecular oxygen by metalloenzymes are not at present well understood,[4] and any information concerning the reactivity of O_2 bonded to metals is therefore highly relevant. We consider in this paper the reactivity of the O_2-group in μ-peroxo- and μ-superoxo-dicobalt(III) complexes with SO_2 and NO.[5] The μ-peroxo-series of complexes may be regarded as oxygen carriers.[6] Crystal structures of both types of complex have been determined.[7] Also of interest is whether single-bridged μ-sulphato-dicobalt(III) complexes can be prepared by reacting μ-peroxo-complexes with SO_2.

Formulae of μ-peroxo-complexes (*A*)—(*I*), and μ-superoxo-complexes (*J*) and (*K*) used in the present investigation are displayed.

Double-bridged Complexes with SO_2.—Reactions of two μ-amido-μ-peroxo-complexes, (*A*) and (*B*), and the μ-hydroxo-μ-peroxo-complex (*C*) were studied. A comparison was made of the effectiveness of the treatment with gaseous SO_2, liquid SO_2, and SO_2 in aqueous solution media.

Brown to red colour changes were apparent within a few hours in the gas-phase treatment, and 90% conversion of (*A*) was observed over a 9 h period, where unchanged μ-peroxo-complex was determined spectrophotometrically at *ca.* 700 nm following oxidation to the corresponding μ-superoxo-complex with cerium(IV) or chlorine. The μ-amido-μ-hydroxo-complex, $[(NH_3)_4Co{\cdot}\mu(NH_2,OH){\cdot}Co(NH_3)_4]Br_4$,[8] does not react with SO_2 in the gas-phase, and it is unlikely therefore that the hydroxo-bridge of (*C*) is reactive. Reaction occurred more readily on treatment with liquid SO_2 at −10°. The complexes were soluble in liquid SO_2 and brown to red colour changes were observed in the early stages (*ca.* 30 min). The SO_2 was allowed to evaporate off under anhydrous conditions. To ensure complete conversion a second treatment was carried out. The same

---

[1] L. Vaska, *Science*, 1963, **140**, 809; R. W. Horn, E. Weissberger, and J. P. Collman, *Inorg. Chem.*, 1970, **9**, 2367.

[2] J. Valentine, D. Valentine, and J. P. Collman, *Inorg. Chem.*, 1971, **10**, 219.

[3] J. J. Levison and S. D. Robinson, *J. Chem. Soc.* (*A*), 1971, 762.

[4] R. O. C. Norman and J. R. L. Smith, ' Oxidases and Related Redox Systems,' vol. 1, eds. T. E. King, H. S. Mason, and M. Morrison, Wiley, New York, 1965, p. 131.

[5] A. G. Sykes and J. A. Weil, *Progr. Inorg. Chem.*, 1970, **13**, 1—106.

[6] See for example S. Fallab, *Chimia*, 1967, **21**, 538; 1969, **23**, 177.

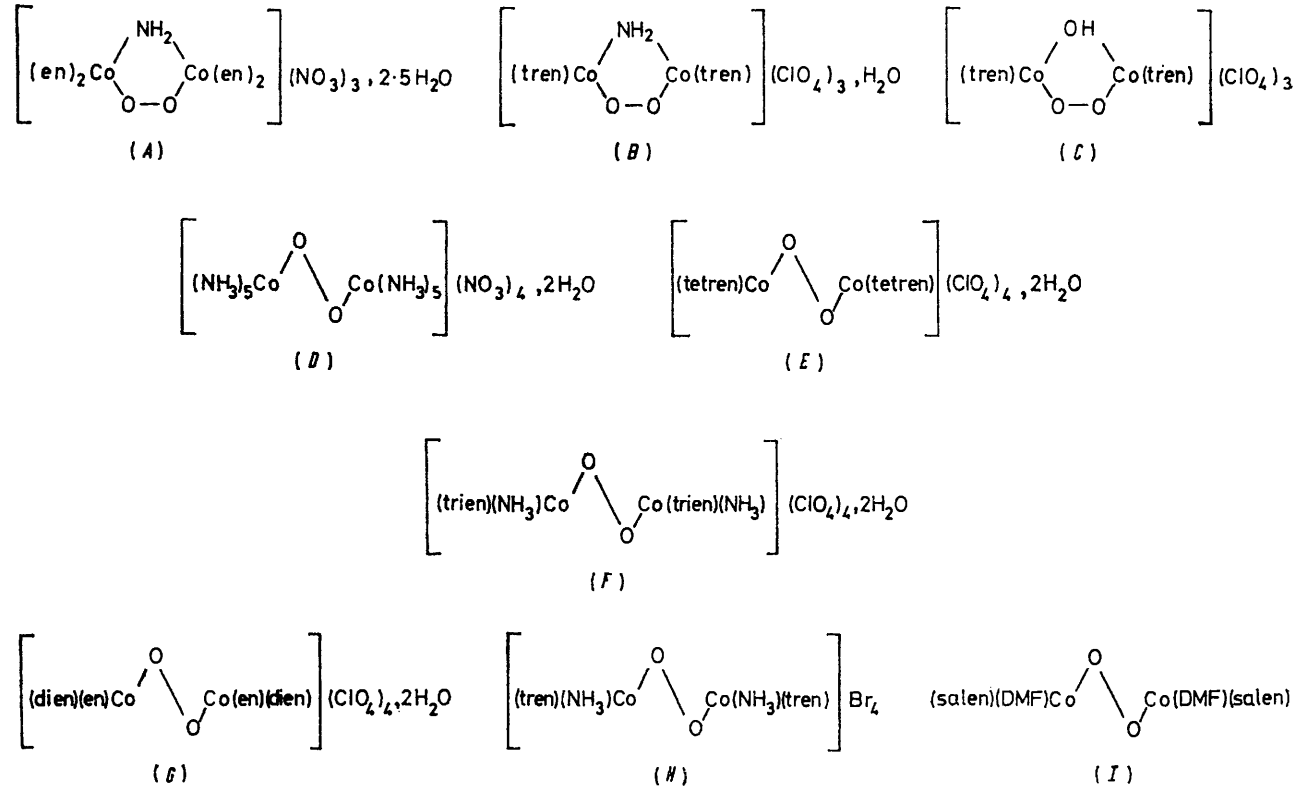
[7] Data obtained by R. E. Marsh, W. P. Schaefer, and U. Thewalt are summarized in ref. 5, p. 6.

[8] S. W. Foong, Ph.D. Thesis, University of Leeds, 1971.

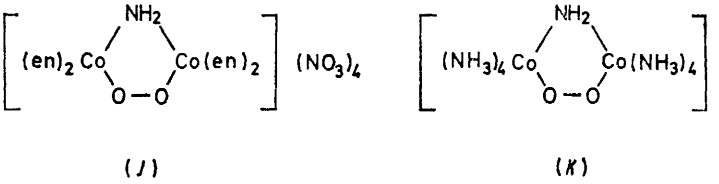
products were obtained from the gas-phase and liquid-phase reactions. These were recrystallized from aqueous (acidic) media.

In the case of (*A*) the product is the known μ-amido-μ-sulphato-complex $[(en)_2Co{\cdot}\mu(NH_2,SO_4){\cdot}Co(en)_2](NO_3)_3$,[9] $\lambda_{max.}$ 523 nm, ε 374 l mol^{-1} cm^{-1}. With (*B*) the μ-amido-μ-sulphato-product $[(tren)Co{\cdot}\mu(NH_2,SO_4){\cdot}Co(tren)](ClO_4)_3,2H_2O$, $\lambda_{max.}$ 528 nm, ε 868 l mol^{-1} cm^{-1}, has not previously been prepared. Spectrophotometric changes indicate that the μ-hydroxo-μ-sulphato-complex is the primary product from (*C*), but in aqueous solution the behaviour observed was not entirely consistent with this assignment, and some μ-hydroxo-cleavage is believed to occur. Equation (1) is we believe an adequate summary of the primary reaction occurring in all three cases.

$$\mu(O_2^{2-}) + SO_2 \longrightarrow \mu(SO_4^{2-}) \qquad (1)$$



μ-Peroxo-complexes: en = ethylenediamine; dien = diethylenetriamine; tren = 2,2′2″-triaminotriethylamine; trien = triethylenetetra-amine; tetren = tetraethylenepenta-amine; salen = *N,N′*-ethylenebis(salicylideneimine); DMF = dimethylformamide



μ-Superoxo-complexes; en = ethylenediamine

The complexes (*A*)—(*B*) are stable in aqueous solution pH 2—7, under which conditions (*A*) at least is unprotonated.[10] No reaction is observed on treatment with aqueous sodium sulphite, pH *ca.* 6. However with the further addition of $HClO_4$, pH 2, rapid brown to red colour changes are observed consistent with the formation of μ-sulphato-complexes as in (1). If alternatively SO_2 is bubbled through an aqueous solution of complex, H_2SO_3 (or more precisely SO_2,xH_2O) [11] is formed, the pH decreases to < *ca.* 6, and the same reaction is observed. With (*C*) decomposition to cobalt(II) with the release of oxygen is observed at pH 2.

Finally the double-bridged μ-amido-μ-superoxo-complexes (*J*) and (*K*) do not react with SO_2 in the gas phase. Addition of aqueous sodium sulphite to (*J*)

---

[9] A. Werner, *Annalen*, 1910, **375**, 53; Y. Sasaki, J. Fujita, and K. Saito, *Bull. Chem. Soc. Japan*, 1969, **42**, 146; A. G. Sykes and M. B. Stevenson, *J. Chem. Soc.* (*A*), 1969, 2979.

[10] For details of protonation of (*A*) see M. Mori and J. A. Weil, *J. Amer. Chem. Soc.*, 1967, **89**, 3732.

[11] See for example F. A. Cotton and G. Wilkinson, ' Advanced Inorganic Chemistry,' 3rd edn., Wiley, 1972, p. 447.

(which is stable at pH *ca.* 6) results in rapid colour changes (green ⟶ red/brown). Under air-free conditions equivalent amounts of (*A*) and the μ-amido-μ-sulphato-complex are formed.[12] Little or no reaction of (*A*) with sulphite is observed under these conditions of pH. Whereas protonation of the complex and/or sulphite is crucial to the reaction of the peroxo-complex (*A*), the superoxo-complex (*J*) reacts most readily with SO_3^{2-} ions.[12] It has been observed that (*J*) and (*K*) react with liquid SO_2 and extensive formation of the μ-amido-μ-sulphato-complexes is observed after treating 1—2 times.

Single-bridged Complexes with SO_2.—The μ-peroxo-group in the single-bridged situation reacts much less readily with SO_2. Five amine complexes (*D*)—(*H*) were investigated. Of these (*D*) could not be purified by recrystallization,[13] and had to be used within 1 h of preparation. Addition of SO_2 in the gas-phase treatment was slow, the most favourable reaction time being *ca.* 80 h for (*E*), and this approach did not seem to merit further investigation. No reaction was observed on treatment of complexes (*E*)—(*H*) with aqueous sodium sulphite, pH *ca.* 6. At this pH (*D*) decomposes. On decreasing the pH complexes (*E*)—(*H*) also decompose giving cobalt(II) and oxygen, and no reaction with sulphite was observed.

Experiments with liquid SO_2 yielded the most significant results, and brown to red colour changes were generally observed during the first/second treatment. After treating 5—8 times with liquid SO_2 the μ-peroxo-content was generally <1%. Although in the case of (*G*) and (*H*) difficulties were experienced due to insolubility of the reactant and/or product, surface colour changes clearly indicated some reaction. Single-bridged sulphato-complexes are we believe formed, equation (1). Analyses of the products from (*E*) and (*F*) indicated one sulphur atom per two cobalt atoms, and the reactions are not therefore of the same kind as referred to in ref. 14. We did not succeed in fully characterizing any one product however, and supporting evidence is fragmentary. For example strong i.r. evidence was obtained for bridging sulphate in the product from (*D*), and strong ν_3 bands were observed at 1030, 1120, and 1190 cm^{-1} (ν_1 at 972 cm^{-1}) indicating sulphate with C_{2v} symmetry.[15] A band as high as 1190 cm^{-1} is not generally observed for monodentate or unco-ordinated sulphate. Other samples were sensitive to atmospheric moisture and the i.r. spectrum of the bromide salt from (*H*) changed during recording (Nujol mull). Attempts to recrystallize the adduct formed with the tetren complex (*E*) and to convert to other than a perchlorate salt were unsuccessful, and at pH < 2 we conclude that this and other complexes aquate to give monomeric species. Ion-exchange separation of a solution of the tetren product using Dowex 50W-X12 resin gave two fractions. The first which was eluted with 1·5M-$HClO_4$ gave a precipitate on standing with Ba^{2+} ions, and is we believe Co(tetren)-SO_4^+. The second which was eluted with 2·5M-$HClO_4$ did not give a positive test for sulphate and is most likely Co(tetren)H_2O^{3+}. Both fractions underwent subsequent aquation/isomerization reactions over a period of days at room temperature to give identical products having u.v.–visible absorption peaks at 355 and 486 nm similar to those reported in ref. 16. In theory four isomeric forms of Co(tetren)H_2O^{3+} are possible.

Further studies with the Schiff's base complex (*I*) indicated a black to dark green colour change after treatment with SO_2 gas. Attempts to characterize the product were unsuccessful, and from analyses the addition of more than one SO_2 is possible. On treatment with with liquid SO_2 the complex undergoes decomposition.

Other μ-Sulphato-complexes.—Hertzenberg and Bailar[17] have observed that single-bridged μ-sulphato-complexes prepared using thermogravimetric techniques are unstable in the presence of H_2O. Since we were unable to prepare stable single-bridged μ-sulphato–complexes and isolate these from aqueous solutions we thought it relevant to check the authenticity of the single-bridged μ-sulphato-bis[triamminedinitritocobalt(III)] complex $[(NO_2)_2(NH_3)_3Co{\cdot}SO_4{\cdot}Co(NH_3)_3(NO_2)_2],2H_2O$ which was reported in 1934.[18] We have repeated the procedure as described by Meyer *et al.*, and found analyses to be in agreement with the above formula. However the two water molecules were retained after standing the sample over P_2O_5 *in vacuo* for 4 days and i.r. bands, in particular the single strong ν_3 band at 1075 cm^{-1}, clearly do not support a structure in which the sulphate is monodentate or bridging. Nor is the relatively high solubility in water consistent with a complex of zero charge. Our experiments clearly indicate an alternative formulation $[Co(NH_3)_3(NO_2)_2(H_2O)]_2SO_4$. The complex has an orange colour and gives $\lambda_{max.}$ 460 nm, $\varepsilon_{max.}$ 135 l mol^{-1} cm^{-1} (per cobalt), in 0·1M-perchloric acid. A chloride salt was prepared and gave the same visible range spectrum in 0·1M $HClO_4$; an i.r. spectrum confirmed that the sample was free from sulphate.

Reactions with Nitric Oxide.—When NO is bubbled through an aqueous solution of (*A*) at room temperature, pH *ca.* 6, the well characterized μ-amido-μ-nitrito-complex $(en)_2Co{\cdot}\mu(NH_2,NO_2){\cdot}Co(en)_2^{4+}$, $\lambda_{max.}$ 473 nm, ε 326 l mol^{-1} cm^{-1},[5,9,19] is obtained within 1—2 h, (2).

$$\mu(O_2^{2-}) + 2NO \longrightarrow \mu(NO_2^-) + NO_2^- \qquad (2)$$

The reaction is more rapid at lower pH. A mechanism

---

[12] J. D. Edwards, C. Y. Yang, and A. G. Sykes, to be published.

[13] M. Mori, R. Davies, A. G. Sykes, and J. A. Weil, *Inorg. Synth.*, 1970, **13**; M. Mori, J. A. Weil, and M. Ishiguro, *J. Amer. Chem. Soc.*, 1968, **90**, 615.

[14] T. Shibahara and M. Mori, *Bull. Chem. Soc. Japan*, 1972, **45**, 1437.

[15] K. Nakamoto, J. Fujita, S. Tanaba, and M. Kobayashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4904; N. Tanaka, H. Sugi, and J. Fujita, *Bull. Chem. Soc., Japan*, 1964, **37**, 640; K. Wieghardt and J. Eckert, *Z. anorg. Chem.*, 1971, **383**, 240.

[16] D. A. House and C. S. Garner, *Inorg. Chem.*, 1967, **6**, 272.

[17] E. P. Hertzenberg and J. C. Bailar, *Inorg. Chem.*, 1971, **10**, 2371.

[18] J. Meyer, G. Dirska, and F. Clemens, *Z. anorg. Chem.*, 1934, **139**, 330.

[19] A. Werner, *Annalen*, 1910, **375**, 54.

involving direct NO attack of the μ-peroxo-bridge is implied. Sodium nitrite on the other hand does not react with (*A*) overnight at pH *ca.* 6, and this reaction is also relatively slow at pH 3·5. The reaction of NO with (*J*) at pH *ca.* 6, gives first (*A*), (3), reaction complete *ca.* 5 min at room temperature, which is then further

$$\mu(O_2^-) + NO \longrightarrow \mu(O_2^{2-}) + NO^+ \qquad (3)$$

reduced as in (2). The rate of reaction of (*J*) is about the same in 0·4M-$HClO_4$, but under these conditions (due to the relative rates) no evidence was obtained for the intermediate formation of (*A*) in the conversion through to the μ-amido-μ-nitrito-product.

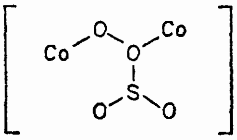
Slow reactions, *ca.* 50% conversionin 6 days, were observed between NO gas and solid samples of the μ-amido-μ-peroxo-complex (*A*) and the μ-amido-μ-superoxo-complex (*J*). The product–reactant mixture from (*A*) is orange-brown, and that from (*J*) a red-grey colour. These reactions and products were not investigated further due to the slowness of the changes.

DISCUSSION

Conditions favouring the addition of SO_2 to the O_2-bridge may be summarized as follows. Treatment with liquid SO_2 is more favourable than treatment with SO_2 in the gas phase. The rate of the reaction in aqueous solution is dependent on pH, the faster rates being observed at low pH's, when reaction proceeds at a comparable rate to that in liquid SO_2. No reaction is observed however at pH's *ca.* 6·0.

Complexes containing a second bridge in addition to the μ-peroxo-group react more readily than those containing a single μ-peroxo-bridge. This can be rationalized by a consideration of *X*-ray crystal structures of μ-peroxo-complexes.[5] The oxygen atoms are σ-bonded to the cobalt atoms which are held in positions *cis* to each other in the double-bridged complexes, but take up *trans* positions in the single-bridged complexes. Similar structures are believed to be present also in solution, and the decrease in reactivity of single-bridged complexes can therefore be explained in terms of steric hindrance due to the positioning of the two cobalt co-ordination spheres.

Formation of co-ordinated sulphate is observed in all the μ-peroxo-reactions but that of (*I*), details of which appear more complicated. The i.r. spectrum of the product from (*D*) clearly indicates the presence of a μ-sulphato-ligand. The possibility that reactions of single-bridged μ-peroxo-complexes with SO_2 do not always yield a μ-sulphato-product has been considered. Thus addition of SO_2 to give an intermediate, with bonding as illustrated, if followed by O–O cleavage is unlikely to yield a binuclear product, unless a second bridging group is present which will give the complex the opportunity to reform a second (sulphato) bridge. The full stoicheiometric and mechanistic implications of an O–O cleavage in the case of the single-bridged complexes are not clear however (since further steps are necessary), and without further information an intramolecular rearrangement to give μ-sulphato-complexes as primary products seems far more reasonable. The net reaction corresponds to insertion of SO_2 into the μ-peroxo-bridge.



The loss of sulphate from the double-bridged complex $(NH_3)_4Co{\cdot}\mu(NH_2,SO_4){\cdot}Co(NH_3)_4^{3+}$, is known to be catalysed by hydrogen ions,[20] but this process is by no means fast possibly due to the rapidity of sulphate-bridge reformation prior to cleavage of the second $CoOSO_3$ bond. Single-bridged μ-sulphato-complexes are we believe labile in aqueous media because protonation of the sulphato-bridge results in irreversible cleavage in the absence of a second-bridging ligand.

The reactivity of two μ-superoxo-complexes with SO_2 has also been investigated. Striking differences are observed in comparisons with μ-peroxo-complexes. The μ-superoxo-complexes do not react with SO_2 *in* the gas phase, and in aqueous solution react with SO_3^{2-} ions.[12] The reactions of complexes (*J*) and (*K*) with liquid SO_2 while slower than with the corresponding μ-peroxo-complexes proceed at an appreciable rate. A possible reaction sequence is $\mu(O_2^-) \longrightarrow \mu(O_2^{2-}) \longrightarrow \mu(SO_4^{2-})$.

The reactions of μ-peroxo- and μ-superoxo-complexes with NO have been less estensively studied. Observations on the reactions of (*A*) and (*J*) are probably typical of the double-bridged complexes at least. Formation of the μ-amido-μ-nitrito-complex is observed. Whereas free oxygen reacts with NO to give NO_2 the NO is less extensively oxidized (to NO_2^-) when the oxygen is complexed. Reduction of the μ-amido-μ-superoxo-complex by NO in aqueous solution, equation (2), involves direct bonding of the reductant to the μ-peroxo-bridge. The product is the μ-amido-μ-nitrito-complex, in which the NO_2 group is bonded *via* an O-atom to one cobalt and *via* an N-atom to the other. Intermediate formation of a μ-nitrito-complex in which both oxygen atoms are bonded to cobalt (Co–O–N–O–Co), or a dinitrito-complex, or an aquo-nitrito-complex (the latter two having only a single μ-amido-bridge) is necessary to account for the formation of this product. Unfortunately none of these intermediates has been prepared, and it has not been possible therefore to test which mechanism might apply. A dinitro-product has been identified in corresponding reactions of dioxygen complexes of platinum metals.[3] It is interesting to speculate whether the extremely slow reaction of NO gas with a solid sample of the μ-amido-μ-superoxo-complex yields the μ-amido-μ-nitrato-complex by direct addition, (4). There is no evidence in aqueous

$$\mu(O_2^-) + NO \longrightarrow \mu(NO_3^-) \qquad (4)$$

---

[20] M. B. Stevenson, A. G. Sykes, and R. S. Taylor, *J. Chem. Soc.* (*A*), 1970, 3214.

solutions for the formation of such a species and reduction to the corresponding μ-peroxo-complex is observed, most probably by a non-bonded (*i.e.* outer-sphere) mechanism. Reactions of (*A*) and (*J*) with NO_2 to give the same μ-amido-μ-nitrito-product have previously been reported by Garbett and Gillard.[21]

Finally it is perhaps appropriate to comment on some general features of reactions of μ-peroxo- and μ-superoxo-complexes. It is clear from the information listed in Table 4 of ref. 22 that μ-peroxo-complexes prefer to bond directly to a reductant, whereas in the reactions of μ-superoxo-complexes such a close approach of reactants does not occur. A further point is the preference of μ-peroxo-complexes for reaction with protonated oxy-anions, contrast μ-superoxo-complexes which react preferentially with unprotonated species. Results obtained in this work are consistent with these emerging patterns of behaviour.

EXPERIMENTAL

Details of the preparation of the μ-peroxo-complexes are to be found as follows (*A*) (ref. 10); (*B*), (*C*), and (*H*) (ref. 23); (*D*) (ref. 13); (*E*), (*F*), and (*G*) (ref. 24); and (*I*) (ref. 25). Standard Schlenk tube techniques were used in the latter. The amine ligands used were as follows: tetraethylenepenta-ammine (Koch–Light), triethylenetetra-amine (Emanuel), diethylenetriamine (Koch–Light), 2,2′,2″-triaminotriethylamine (Fluka), and ethylenediamine (Hopkin and Williams). The ligand salen was prepared by the method in ref. 26. The two μ-superoxo-complexes were prepared according to details in ref. 13. The identity of samples obtained was confirmed by elemental analyses and/or reference to published details of u.v.–visible spectra.

The nitro-cobalt(III) complex $[Co(NH_3)_3(NO_2)_2(H_2O)]_2$-$SO_4,2H_2O$ was prepared (Analysis found: H, 4·2; S, 5·9; calc. H, 4·1; S, 5·97%) using the procedure previously reported for the μ-sulphato-complex $[(NH_3)_3(NO_2)_2Co{\cdot}SO_4{\cdot}Co(NO_2)_2(NH_3)_3],2H_2O$.[18] A sample of the nitro-complex $[Co(NH_3)_3(NO_2)_3]$ [27] was first converted to the red-brown complex $[Co(NH_3)_3(NO_2)_2Cl]$ [28] by treating with concentrated HCl diluted 1 : 1. Orange coloured crystals were obtained on treatment with dilute H_2SO_4. A sample of the chloride salt $[Co(NH_3)_3(NO_2)_2(H_2O)]Cl$ was prepared from the sulphate salt.

Reactions with SO_2 were studied by gas phase, liquid phase, and aqueous solution phase methods. The gas-phase method consisted of passing SO_2 at a very slow rate (<10 bubbles min^{-1} as measured at exit) through a reaction tube with an open boat containing a finely ground sample (*ca.* 0·2 g) of complex. Samples of complex were dried *in vacuo* over P_2O_5 in desiccator prior to use, and care was taken to keep samples dry throughout the reaction tube (entry and exit drying tubes containing P_2O_5 and $CaSO_4$ respectively were used). The apparatus was flushed with nitrogen gas prior to use, all tubing was of PVC plastic.

The liquid-phase treatment was carried out in a Dewar reaction flask. Sulphur dioxide gas was condensed onto a sample of complex in the Dewar by passing it through a spiral glass tube immersed in solid CO_2–acetone. The Dewar tube was filled about three-quarters full (30 ml), and the SO_2 then left to evaporate (*ca.* 8 h). The SO_2 gas was dried by passing through a tube of silica gel; a drying tube of P_2O_5 was used to protect the exit tube. Samples obtained by this and the gas phase method were freed from traces of SO_2 gas by leaving in a desiccator *in vacuo* for 1—2 days.

Analyses for the complex $[(tren)Co{\cdot}\mu(NH_2,SO_4){\cdot}Co(tren)]$-$(ClO_4)_3,2H_2O$ were as follows (Found: C, 17·2; H, 5·0; N, 14·8; S, 3·55. Calc. C, 16·8; H, 4·9; N, 14·7; S, 3·73%).

In the aqueous solution experiments a brisk stream of SO_2 was passed through reactant solutions contained in a 4 cm optical cell.

Nitric oxide (Matheson, technical quality cylinder gas) is more difficult to condense, and the gas phase and aqueous solution procedures only were investigated. Unlike SO_2 there is no reaction of NO with the aqueous media; the gas is however less soluble.

We are most grateful to Dr. D. C. Goodall for advice and the loan of apparatus in connection with the liquid-phase SO_2 treatment. Dr. K. Wieghardt suggested the experiments relating to the work described in ref. 18, and Professor H. Siebert generously supplied a sample of the complex $Co(NH_3)_3(NO_2)_3$. Assistance from Dr. Y. Sasaki and Mr. P. J. M. O'Neill is also acknowledged.

[3/2401 *Received, 23rd November, 1973*]

---

[21] K. Garbett and R. D. Gillard, *J. Chem. Soc.* (*A*), 1968, 1725.

[22] A. G. Sykes, *Chem. in Britain*, **1974**, 170.

[23] C. H. Yang and M. W. Grieb, *Inorg. Chem.*, 1973, **12**, 663.

[24] D. L. Duffy, D. A. House, and J. A. Weil, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2053.

[25] C. Floriani and F. Calderazzo, *J. Chem. Soc.* (*A*), 1969, 946.

[26] R. H. Bailes and M. Calvin, *J. Amer. Chem. Soc.*, 1947, **69**, 1886.

[27] M. Linhard and H. Siebert, Anorganisch Chem. Institut, Heidelberg University, unpublished work.

[28] S. M. Jorgensen, *Z. anorg. Chem.*, 1894, **7**, 310.