TABLE V
THE AFFINITY OF BOUND LIGANDS FOR EXTERNAL REAGENTS AT 25.0°

Complex (Co(III))	K_1, M^{-1}		
	Hg^{2+} [a]	H^+ [b]	Ref
$Co(NH_3)_5X$	9.9×10^4	1.7×10^6	33
trans-$Co(en)_2H_2OX$	2.2×10^4	1.4×10^4 [c]	34
cis-$Co(en)_2NO_2X$	6.6×10^5	2.0×10^6	35
trans-$Co(en)_2ClX$	1.3×10^5	1.3×10^6 [d]	36

[a] Refers to the equilibrium $Hg^{2+} + CoL_5X^{n+} = CoL_5XHg^{(n+2)+}$. [b] Refers to the equilibrium $H^+ + CoL_5OH^{n+} = CoL_5OH_2^{(n+1)+}$. [c] Corrected for statistical factor. [d] At 20°.

If it is assumed that changing the X group in CoL_5X^{n+} does not affect the trends seen in Table V, then the data can be used to assess the importance of precursor complex formation on studies in which the variation is made remote from the reaction center, variations in "nonbridging" ligands. We consider here two selected examples of such application. (1) The rates of Hg^{2+}-assisted aquations of chloro complexes of Co(III) have been correlated with the rate of spontaneous aquation.[5] The underlying assumption in this correlation was that precursor complex stability varied only slightly as the "nonbridging" ligands were varied. The deviation of *trans*-$Co(en)_2H_2OCl^{2+}$ from the correlation noted is now reasonably explained on the basis of the instability of the complex *trans*-$Co(en)_2H_2OClHg^{4+}$ relative to the precursor complexes of the other chloro compounds. (2) The second area in which these results are of consequence is in the consideration of precursor complexes in inner-sphere electron-transfer reactions.[8-10] Our results imply that studies of nonbridging ligand effects in inner-sphere electron-transfer processes need consider at most a 3 kcal mol^{-1} variation in precursor stability (for nonbridging ligands of the type studied herein). Hence models in such studies are not highly sensitive to variable precursor stabilities.

On the other hand, the data presented can usefully be compared with those in an earlier paper[5] to demonstrate that the formation constant of complexes of the type L_5CoXHg^{n+} are quite sensitive to the nature of X. From the lack of deviation of second-order kinetics in the reaction of Hg^{2+} with $Co(NH_3)_5Cl^{2+}$,[5] an upper limit of 10 M^{-1} can be placed on K for $Hg^{2+} + Co(NH_3)_5Cl^{2+} = Co(NH_3)_5ClHg^{4+}$. This number is to be compared with 9.9×10^4 M^{-1} for the corresponding reaction with NCS^- as the bridging group. On the other hand, reference to Table V indicates it is unlikely that the equilibrium constants for Cl^- and NCS^- binding to Hg^{2+} differ by more than a factor of 10^2. Thus the relative interaction of Hg^{2+} with these two ligands is a sensitive function of whether the ligand is bound to Co(III) or not. Such variations are likely to make arguments about rate patterns based on the precursor complex as a starting point dangerous unless care is taken to establish these stabilities.

Acknowledgments.—This research was financed partially by the Public Health Service (Grant GM-14830) and partially by the Committee on Research of the Academic Senate, University of California, San Diego, La Jolla, Calif. We are grateful for that support. We thank Jim Sullivan for many helpful comments.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF STANFORD UNIVERSITY, STANFORD, CALIFORNIA 94305,
AND PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY 08540

The Formation of Chelated Sulfate by Reactions between Sulfur Dioxide and Oxygen in the Coordination Sphere of Iridium and Ruthenium Complexes

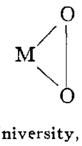
BY JOAN VALENTINE,[1] DONALD VALENTINE, JR.,[1] AND JAMES P. COLLMAN*[2]

Received June 17, 1970

Organo transition metal complexes containing bidentate sulfate may be prepared by adding SO_2 to MO_2 complexes or by adding O_2 to MSO_2 complexes. The scope of these reactions is discussed and new examples are reported for iridium, rhodium, and ruthenium complexes.

Introduction

Over the past few years several mononuclear diamagnetic oxygen complexes have been prepared through oxidative addition of O_2 to basic transition metal compounds.[3] Many of these complexes have been shown to have triangular structures in which the O–O bond distance is greatly increased in comparison with free O_2.[4]



A significant aspect of these complexes is the greater reactivity of coordinated oxygen toward reductants.[5] A broad class of oxygenases which occupy a central role in biology are metalloenzymes which apparently make use of metal-activated molecular oxygen.[6] The de-

---

[1] On leave from Princeton University, spring 1969.

[2] Author to whom inquiries may be addressed at Stanford University.

[3] L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968).

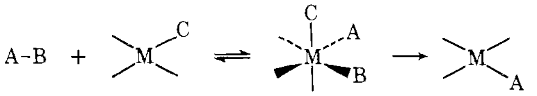
[4] J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, **91**, 6301 (1969), and references therein.

[5] J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

[6] R. O. C. Norman and J. R. L. Smith, "Oxidases and Related Redox Systems," Vol. 1, T. E. King, H. S. Mason, and M. Morrison, Ed., Wiley, New York, N. Y., 1965, p 131.

tailed mechanisms by which these enzymatic reactions take place are at present poorly understood. Metal surfaces[6] also catalyze autoxidation of substrates through chemisorption of molecular oxygen—one example being the conversion of SO_2 to SO_3 in the platinum-catalyzed contact process used to manufacture sulfuric acid.[7]

Our interest in reactions of coordinated molecular oxygen derives from the realization that a broad class of atom-transfer redox reactions can be promoted by a metal which holds both reductant and oxidant in adjacent coordination sites.[8] Such processes (eq 1) can be imagined to embody as discrete steps oxidative addition, migratory insertion, and reductive elimination. If ligand replacement of the reduced fragment A by the reductant C occurs (eq 2), the overall reaction becomes catalytic (eq 3).

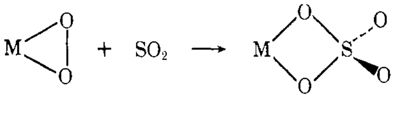

(1)

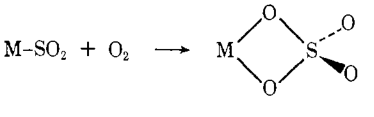

(2)

$$\underset{\text{oxidant}}{\text{A-B}} + \underset{\text{reductant}}{\text{C}} \xrightarrow{\text{M catalyst}} \text{B-C} + \text{A} \qquad (3)$$

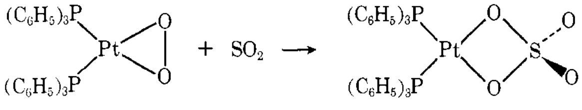
After discovering both catalytic and stoichiometric examples of metal-promoted atom-transfer redox reactions in which azides act as oxidants,[8] our attention was drawn to the more important case of molecular oxygen.

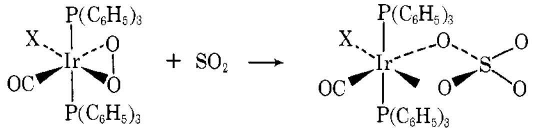
This paper describes a series of reactions between O_2 and SO_2 which take place at a metal complex to form coordinated sulfate. Such reactions can be carried out in two modes: either by starting with coordinated oxygen and free SO_2 (eq 4) or by allowing free O_2 to react with coordinated SO_2 (eq 5). In our experience, the first reaction (eq 4) always takes place, but the success of the second path (eq 8) seems to depend on the particular system.

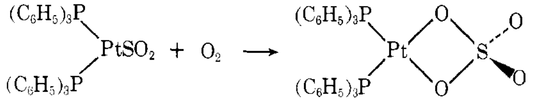

(4)


(5)

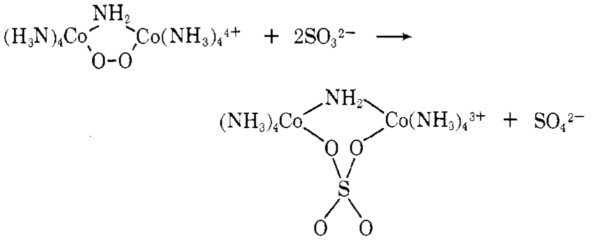
A number of examples of reaction 4 and at least one example of reaction 5 have been previously reported.[5,9] For instance, the platinum-oxygen complex **1** and the iridium-oxygen complex **3** both react with SO_2 to give the corresponding sulfates **2** and **4** (eq 6 and 7), while the platinum-sulfur dioxide complex **5** reacts with O_2 to give the sulfate **2** (eq 8).


1 **2** (6)


3a, X = Cl
b, X = Br
c, X = I
4 (7)


5 **2** (8)

These reactions may also be related to that of sulfite ion with μ-superoxo-μ-amido-bis[tetraamminecobalt-(III)](4+) (eq 9).[10]


(9)

The mechanism of reaction 7 has been partially clarified through a study employing ^{18}O isotopic labeling.[11] The scope of reactions 4 and 5 is the subject of this paper.

Results and Discussion

The iridium-oxygen complexes **3** each react smoothly with SO_2 in solution or in the solid state to form the iridium sulfate **4**. The chlorosulfato complex **4a** was also prepared by treating $IrCl(CO)(P(C_6H_5)_3)_2$, **6**, with H_2SO_4 in tetrahydrofuran (eq 10). The latter reaction, which serves to establish unambiguously the presence of the sulfate ligand, is slow and a hydrido intermediate having ir bands at 2260 cm^{-1} was detected prior to formation of the sulfate **4a**.

$$IrCl(CO)(P(C_6H_5)_3)_2 + H_2SO_4 \longrightarrow \textbf{4a} \qquad (10)$$

The air-stable, sparingly soluble crystalline sulfates **4** were characterized by elemental analysis and ir spectra. All of the sulfato complexes described herein exhibit bands in the regions 1300–1250, 1170–1150, 900–850, and 660–610 cm^{-1} (Table I). The assignment of these absorptions to the sulfato ligand were confirmed in **2** and **4** by isotopic substitution studies.[11] A

---

[7] L. C. Schroeter, "Sulfur Dioxide," Pergamon Press, Oxford, 1966, p 34.

[8] J. P. Collman, M. Kubota, and J. W. Hosking, *J. Amer. Chem. Soc.*, **89**, 4809 (1967).

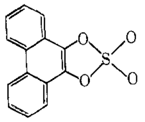
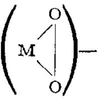
[9] (a) C. D. Cook and G. S. Jauhal, *ibid.*, **89**, 3066 (1967); (b) N. H. B. Stiddard and R. E. Townsend, *Chem. Commun.*, 1372 (1969); (c) J. J. Levison and S. D. Robinsen, *ibid.*, 198 (1967).

[10] A. G. Sykes and R. D. Mast, *J. Chem. Soc. A*, 784 (1967).

[11] R. W. Horn, E. Weissberger, and J. P. Collman, *Inorg. Chem.*, **9**, 2367 (1970).

TABLE I

INFRARED SPECTRA (CM^{-1}) OF COMPLEXES[a]

	ν(CO)	$\nu(SO_2, SO_4)$		Ref
PtL_2SO_2[b,c]		1182, 1149, 1035		*h*
$IrL_2COClSO_2$	2020	1198, 1185, 1048, 559		*i*
$RhL_2COClSO_2$	2034	1214, 1188, 1057		*i*
$RuL_2(CO)_2SO_2$	2002 s, 1938 s	1212 w, 1144 w, 1066 m, 560 w		
$RuL'_2(CO)_2SO_2$[b]	2002 s, 1934 s	1229 w, 1160 vw, 1072 m, 566 w		
$[Ru(NH_3)_4(SO_2)Cl]Cl$		1301, 1278, 1100, 552		*j*
$FeL_2(CO)_2SO_2$[g]	1966 vs, 1907 vs	1215 s, 1073 vs, 1031 s		*k*
PtL_2SO_4		1281, 1155, 879, 659, 609		*l*
$IrL_2COClSO_4$	2045 vs	1298 s, 1170 s, 885 s, 855 s, 670 s, 618 w		
$IrL_2COBrSO_4$	2045 vs	1298 s, 1170 s, 886 s, 855 m, 665 s, 615 w		
IrL_2COISO_4	2040 vs	1295 s, 1169 s, 880 s, 858 m, 661 s, 610 w		
$RuL_2(CO)_2SO_4$	2055 s, 2000 s	1265 m, 1250 m, 1150 s, 905 m, 893 m, 658 s		
$RuL'_2(CO)_2SO_4$	2050 s, 1990 s	1268 m, 1155 s, 893 m, 660 s		
"RhL_2NOSO_4"	1665 s (ν (NO))	1265 s, 1147 vs, 892 s, 645 vs		
		1411, 1213, 1014, 808		
		ν 		
PtL_2O_2		818 (824 sh)[d]	471[e]	
IrL_2COClO_2	2000[c,f]	858[c,f]	633[e]	
IrL_2COBrO_2	1996[c,f]	962[c,f]	629[e]	
IrL_2COIO_2	1995[c,f]	962[c,f]	625[e]	
IrL_3ClO_2		852 m	563 w	
$IrL_3Cl^{18}O_2$		804 m	. . .	

[a] Crystals in pressed KBr disks unless otherwise noted. [b] $L = P(C_6H_5)_3$; $L' = (C_6H_5)_2P(p\text{-}C_6H_4CH_3)$. [c] Nujol. [d] C. D. Cook and G. S. Jauhal, *Inorg. Nucl. Lett.*, **3,** 31 (1967). [e] Reference 9. [f] J. E. Thomasson and A. Wojcicki, *J. Amer. Chem. Soc.*, **90,** 2709 (1968). [g] Cyclohexane. [h] Reference 9a. [i] L. Vaska and S. S. Bath, *J. Amer. Chem. Soc.*, **88,** 1333 (1966). [j] L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, **4,** 1157 (1965). [k] M. Kubota, private communication. [l] Reference 11.

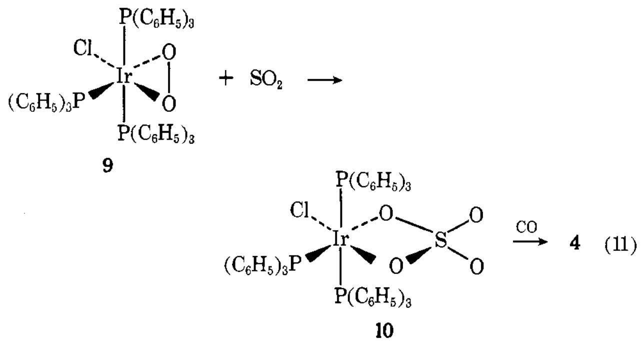
discussion of the infrared spectra of coordinated sulfate is presented elsewhere.[11] On the basis of these infrared studies and the apparent coordinative saturation, we tentatively assign chelated sulfate structures to all of these complexes.

Treatment of the SO_2 complex $IrCl(CO)(SO_2)(P(C_6H_5)_3)_2$, **7**, with O_2 did not lead to any detectable chemical change. This result suggests that both O_2 and SO_2 may need to be in the coordination sphere and that the acidic SO_2 ligand sufficiently reduces the basic character of the central metal to prevent coordination of oxygen.

The analogous rhodium(I) complex, $RhCl(CO)(P(C_6H_5)_3)_2$, does not form a stable O_2 complex. We had hoped the irreversible formation of sulfate might permit us to intercept a rhodium–oxygen complex present in very small concentration. However, neither $RhCl(CO)(P(C_6H_5)_3)_2$ nor the corresponding iodide, which might be expected to form a more stable O_2 adduct,[12] afforded a tractable sulfato complex upon treatment with O_2 and SO_2 under pressure, nor (in the case of the chloride) with H_2SO_4.[13]

The red triphenylphosphine complex, $IrCl(P(C_6H_5)_3)_3$, **8**,[14] afforded a salmon-colored stable O_2 adduct, **9**, which exhibited an ir band at 852 cm^{-1} characteristic of coordinated oxygen. The third phosphine was replaced by CO only at elevated temperatures under high pressure yielding a mixture of $IrCl(O_2)(CO)(P(C_6H_5)_3)_2$ and $IrCl(CO)_2(P(C_6H_5)_3)_2$. This result attests to the stability of the O_2 adduct, **9**, since the trisphosphine complex, **8**, reacts instantly with a stream of CO at room temperature yielding the Vaska complex **6**. Treatment of the O_2 adduct **9** with SO_2 afforded a sulfate **10** (eq 11). The sulfate **10** was unstable with respect to dissociation of one triphenylphosphine. Elemental analyses of **10** indicate a mixture of bis- and trisphosphine derivatives, but the trisphosphine derivative can be obtained from solutions containing excess triphenylphosphine. Treatment of **10** with CO affords the carbonyl sulfate **4** described earlier.

Treatment of solutions containing the trisphosphine



(11)

---

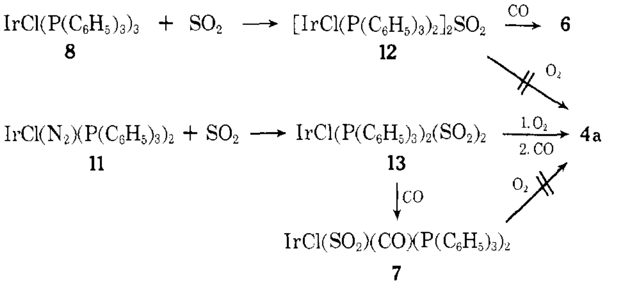
(12) P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88**, 3511 (1966).

(13) Using the ligand $CH_3C(CH_2P(C_6H_5)_2)_3$ (denoted P_3) we have found the SO_2 complex $RhCl(SO_2)P_3$ to react with O_2 to form the sulfate $MCl(SO_4)P_3$, but these results will be presented elsewhere: S. J. Lapporte, W. Siegl, and J. P. Collman, unpublished data.

(14) M. A. Bennett and D. L. Kilmer, *J. Amer. Chem. Soc.*, **91**, 6983 (1969).

complex **8** and the dinitrogen complex **11** with SO_2 led to incompletely characterized yellow and red complexes tentatively assigned structures **12** and **13**, respectively (Scheme I). The similarity between the spectrum of the yellow complex **15** (Table I) and that[15] of $(NC)_5CoSO_2Co(CN)_5^{6-}$ led Kubota[16] to suggest the dimeric structure **12**. The red complex is tentatively assigned structure **13** on the basis of Kubota's[16] work. The yellow complex **12** does not react with O_2 under mild conditions, but the red complex **13** does afford the sulfate **4a** upon successive treatment with O_2 and CO. Each reacts differently with CO (Scheme I).

SCHEME I



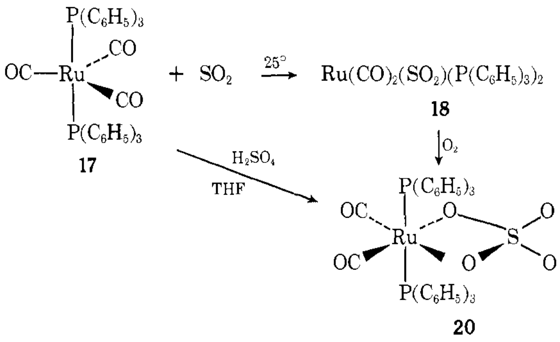
The nitrosyl complexes $RhNO(P(C_6H_5)_3)_3$, **14**, and $IrNO(P(C_6H_5)_3)_3$, **15**, have been shown to undergo some oxidative addition reactions.[17,18] Exposure of solutions containing either **14** or **15** to O_2 did not afford the expected oxygen complexes, but degradative changes took place and triphenylphosphine oxide was formed. Treatment of solutions of **14** and **15** with SO_2 gave reversible color changes, but stable SO_2 adducts could not be isolated. Reaction did occur with mixtures of SO_2 and O_2 affording unstable complexes whose ir spectra showed bands characteristic of bidentate sulfate (eq 12). These sulfates decomposed under attempted recrystallization. Elemental analyses of the crude rhodium complex were most nearly consistent with $Rh(SO_4)(NO)(P(C_6H_5)_3)_2$, **16**, although the carbon analysis was unsatisfactory.

$$\underset{\mathbf{14}}{Rh(NO)(P(C_6H_5)_3)_3} + SO_2 + O_2 \longrightarrow \underset{\mathbf{16}}{Rh(SO_4)(NO)(P(C_6H_5)_3)_2} + P(C_6H_5)_3 \qquad (12)$$

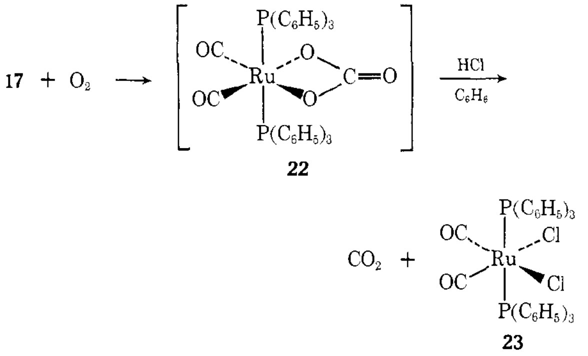
Reactions of SO_2 and O_2 with the five-coordinate d^8 complex $Ru(CO)_3(P(C_6H_5)_3)_2$, **17**, were also examined. Treatment of **17** with SO_2 in benzene at 25° led to the formation of $Ru(CO)_2(P(C_6H_5)_3)_2(SO_2)$, **18**. This facile displacement of CO from the substitution inert five-coordinate d^8 complex is undoubtedly due to the electrophilic character of the amphoteric ligand SO_2[19,20] which can penetrate the saturated coordination sphere by forming a bond with the nonbonding d electrons. The analogous complex $Ru(CO)_2(SO_2)(p\text{-}CH_3C_6H_4P(C_6H_5)_2)_2$, **19**, was prepared similarly. Each SO_2 complex exhibited ir bands characteristic of coordinated SO_2 (Table I). Selected bands for the analogous iron complex $Fe(CO)_2(SO_2)(P(C_6H_5)_3)_2$ are listed for comparison. This iron complex was prepared by irradiating $Fe(CO)_3(P(C_6H_5)_3)_2$ in liquid SO_2.[21] One wonders whether these more vigorous conditions were required because of the reduced basicity of the iron in comparison with ruthenium.

Exposure of the SO_2 complex **18** to air in benzene solutions at 25° afforded a sulfate **20** as a white insoluble complex. The ir spectrum of **20** (Table I) is consistent with its formulation as a bidentate ruthenium(II)–sulfato complex. Using the more soluble bis(diphenyl-*p*-tolyphosphine) complex **19** a similar sulfate, $Ru(SO_4)(CO)_2(p\text{-}CH_3C_6H_4P(C_6H_5)_2)_2$ (**21**), was obtained. The solubility of even **21** was limited, but a molecular weight measurement suggests that it is monomeric The sulfate **20** is better prepared by reaction of **17** with H_2SO_4 in THF.[22] These reactions are illustrated in Scheme II.

SCHEME II



Attempts to form an oxygen complex from **17** resulted in the formation of a carbonate, **22**. Exposure of solid **17** (ν(CO) 1895 cm^{-1}) to the air over a period of months in the dark afforded black crystals having ir bands at 1950, 1980, and 2045 cm^{-1} assignable to CO stretching modes of the Ru(II) complex and strong bands at 1675 and 1635 cm^{-1} which we attribute to a chelated carbonate. Only a trace of triphenylphosphine oxide was observed when the reaction was performed under these conditions. The carbonate was characterized by conversion into the known complex $RuCl_2(CO)_2(P(C_6H_5)_3)_2$, **23**, and CO_2 by treatment with HCl (eq 13).



(13)

---

[15] A. A. Vlcek and F. Basolo, *Inorg. Chem.*, **5**, 156 (1966).

[16] M. Kubota, private communication.

[17] J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Amer. Chem. Soc.*, **91**, 5659 (1969).

[18] C. A. Reed and W. R. Roper, *Chem. Commun.*, 155 (1969).

[19] S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, **5**, 405 (1966).

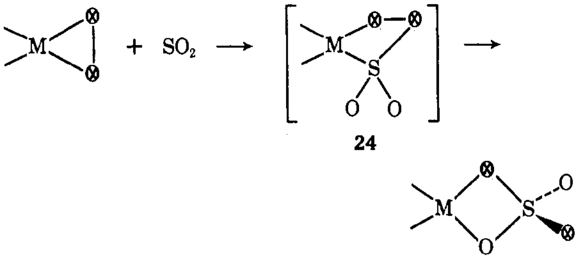
[20] J. E. Thomasson and A. Wojcicki, *J. Amer. Chem. Soc.*, **90**, 2709 (1968).

[21] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc. A*, 2645 (1969).

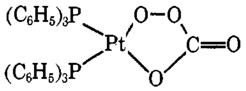
[22] See also K. R. Laing and W. R. Roper, *ibid.*, *A*, 1889 (1969), and references therein.

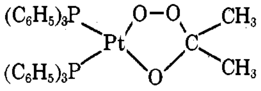
Benzene solutions of **17** reacted gradually with O_2 at 55° but the only tractable product obtained from these was triphenylphosphine oxide. The osmium analog[23] $Os(CO)_3(P(C_6H_5)_3)_2$ is very resistant to aerial oxidation in both solutions and the crystalline state.

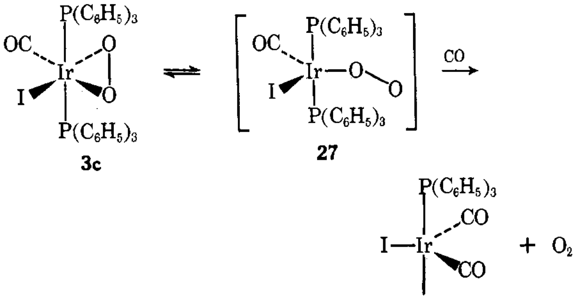
The mechanism of reaction 4 whereby an oxygen complex reacts with SO_2 has been demonstrated in the formation of the iridium sulfate **4** from **3** (eq 7) using ^{18}O labeling.[11] The reaction probably occurs in the manner shown in eq 14 (where ⊗ denotes isotopic labeling) through the formation of a postulated peroxysulfite intermediate, **24**. Strong analogies to this type of intermediate are found in the formation of the peroxycarbonate **25**[24] and pseudoozonide **26**.[25] If one presumes that all examples of reaction 4 go through this path, it follows that the coordinated O_2 molecule must assume a unidentate form at some point along the reaction coordinate. Crumbliss and Basolo[26] have recently described some mononuclear unidentate O_2 complexes (although these have an odd electron). The displacement of O_2 from **3c** by CO to form a saturated dicarbonyl **28** may also be explained by such an intermediate as **27** (eq 15).


24

(14)


25


26


3c **27** **28**

(15)

That SO_2 can attack a saturated coordination shell is well recognized[19] and this may account for the universal success of eq 4, since both SO_2 and O_2 could simultaneously become coordinated to the metal. On the other hand, the reaction between O_2 and a metal seems to require a more basic metal center[27] and this may explain the occasional failures of reactions between MSO_2 complexes and O_2 (eq 5). Furthermore, the role of the SO_2 ligand in the bent[20] or planar form is an unknown factor here. Simultaneous coordination of both reactants, SO_2 and O_2, may not be necessary, but at this time we believe such simultaneous coordination to be required.

Experimental Section

I. **Materials.**—Benzene and tetrahydrofuran were reagent grade chemicals distilled from $LiAlH_4$ and stored under nitrogen. All solvents were deaerated by purging with N_2 or Ar before use. Hi-pure N_2 was passed through a catalyst tube to remove O_2. Matheson Ar, O_2, and SO_2 were used as received. Standard techniques for handling air-sensitive compounds were employed throughout.

II. **Preparation of Complexes.**—The complexes $RuL_2(CO)_3$ [$L = P(C_6H_5)_3$, $P(C_6H_5)_2C_6H_4CH_3$],[28] $Ir(P(C_6H_5)_3)_2(CO)(X)$[29] and $Ir(P(C_6H_5)_3)_2(CO)(X)(O_2)$ ($X = Cl, Br, I$),[12,30] $Ir(P(C_6H_5)_3)_2(CO)(Cl)(SO_2)$,[31] $Ir(P(C_6H_5)_3)_2(Cl)(N_2)$,[32,33] $Ir(P(C_6H_5)_3)_3(Cl)$,[33] $Ir(NO)(P(C_6H_5)_3)_3$,[17] $Rh(NO)(P(C_6H_5)_3)_3$,[17] and $Rh(P(C_6H_5)_3)_2(CO)(X)$ ($X = Cl, I$)[34] were prepared by methods in the literature. The phenanthrene cyclosulfate was prepared following Schenk and Schmidt-Thomee.[35]

1. **Dicarbonylbis(triphenylphosphine)(sulfur dioxide)ruthenium.**—One-fourth gram of $Ru(P(C_6H_5)_3)_2(CO)_3$ was added to 25 ml of tetrahydrofuran saturated with SO_2 at room temperature. A stream of SO_2 was passed through the solution for 1 min, then the flask was allowed to stand for 20 min. The solution was flash evaporated and the residue was kept under high vacuum for 24 hr. An air-sensitive, mustard yellow powder resulted. *Anal.* Calcd for $C_{38}H_{30}P_2O_4SRu$: C, 61.2; H, 4.02; P, 8.33; S, 4.30. Found: C, 59.5; H, 4.2; P, 7.77; S, 4.52.

An analogous procedure gave $Ru(p\text{-}CH_3C_6H_4P(C_6H_5)_2)_2(CO)_2(SO_2)$. *Anal.* Calcd for $C_{40}H_{34}P_2O_4SRu$: C, 62.1; H, 4.40; P, 8.03; S, 4.14. Found: C, 60.0; H, 4.66; P, 7.36; S, 4.13.

2. **Sulfatodicarbonylbis(triphenylphosphine)ruthenium. Method A.**—To freshly prepared $Ru(P(C_6H_5)_3)_2(CO)_2(SO_2)$ was added 20 ml of tetrahydrofuran. The solution was stirred 12 hr in air during which time it became brownish and a white precipitate formed. This was removed by filtration, washed with more tetrahydrofuran, and then vacuum dried.

Method B.—One drop of concentrated H_2SO_4 was added to a mixture of 50 mg of $Ru(P(C_6H_5)_3)_2(CO)_3$ and 5.0 ml of tetrahydrofuran. The solution was allowed to stand for 12 hr. A white precipitate formed and was treated as in method A. Both methods gave $Ru(P(C_6H_5)_3)_2(CO)_2(SO_4)$ having spectra identical with that of authentic material. *Anal.* Calcd for $C_{38}H_{30}P_2O_6SRu$: C, 58.7; H, 3.86; S, 4.12. Found: C, 57.8; H, 4.00; S, 4.27.

An analogous procedure to method A gave crude $Ru(p\text{-}CH_3C_6H_4P(C_6H_5)_2)_2(CO)_2(SO_4)$ which was precipitated from the reaction mixture by adding 20 ml of hexane and cooling for a brief period. The crude product was purified by dissolving it in CH_2Cl_2 and adding hexane until the solution became cloudy. A brown precipitate formed and was discarded. More hexane gave more brown precipitate which also was discarded. Eventually a white precipitate formed. *Anal.* Calcd for $C_{40}H_{34}$-

---

(23) (a) J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, **88**, 3504 (1966); (b) J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, **8**, 419 (1969).

(24) B. J. Hayward, D. M. Blake, C. J. Nyman, and G. Wilkinson, *Chem. Commun.*, 987 (1969).

(25) R. Ugo, F. Conti, S. Cenini, R. Mason, and G. B. Robertson, *ibid.*, 1498 (1968).

(26) A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, **92**, 55 (1970).

(27) J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, **7**, 54 (1968).

(28) J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, **87**, 4008 (1965).

(29) J. P. Collman, C. T. Sears, Jr., and M. Kubota, *Inorg. Syn.*, **11**, 101 (1968).

(30) L. Vaska, *Science*, **140**, 809 (1963).

(31) L. Vaska and S. S. Bath, *J. Amer. Chem. Soc.*, **88**, 1333 (1966).

(32) (a) J. P. Collman and J. W. Kang, *ibid.*, **88**, 3459 (1966); (b) J. P. Collman, M. Kubota, J. Y. Sun, and F. Vastine, *ibid.*, **89**, 169 (1967).

(33) J. P. Collman, M. Kubota, F. D. Vastine, J. W. Kang, *ibid.*, **90**, 5430 (1968).

(34) D. Evans, J. A. Osborn, and G. Wilkinson, *Inorg. Syn.*, **11**, 99 (1968).

(35) G. O. Schenck and G. A. Schmidt-Thomee, *Justus Liebigs Ann. Chem.*, **584**, 199 (1953).

P_2O_6SRu: C, 59.7; H, 4.22; S, 3.98, mol wt 805. Found: C, 58.63; H, 4.45; S, 4.11; mol wt (CH_2Cl_2) 660.

3. **Sulfatochlorocarbonylbis(triphenylphosphine)iridium.**—A concentrated solution of $Ir(P(C_6H_5)_3)_2(CO)(Cl)(O_2)$ in $CHCl_3$ was treated with a slow stream of SO_2 for 15 min. The product was precipitated by addition of CH_3OH, then recrystallized from CH_2Cl_2–CH_3OH mixed solvent. Alternatively, to a solution of 50 mg of $Ir(P(C_6H_5)_3)_2(CO)(Cl)$ in 15 ml of tetrahydrofuran was added 5 drops of concentrated H_2SO_4 and the solution was allowed to stand 12 hr. The solution was concentrated under vacuum, methanol was added, and the precipitate which formed was removed by filtration. The sulfate obtained in this manner was contaminated by small amounts of starting material. When a similar reaction was terminated after 1 hr, the ir spectrum showed a weak band at 2260 cm^{-1} as well as the carbonyl bands due to $Ir(P(C_6H_5)_3)_2COCl$ and $Ir(P(C_6H_5)_3)_2COClSO_4$. Sulfate obtained by the first method was identical with authentic material.

Analogous procedures gave $Ir(P(C_6H_5)_3)_2(CO)(Br)(SO_4)$ and $Ir(P(C_6H_5)_3)_2(CO)(I)(SO_4)$. *Anal.* Calcd for $C_{37}H_{30}P_2SO_5BrIr$: C, 48.2; H, 3.26; S, 3.48; Br, 8.70. Found: C, 48.43; H, 3.42; S, 3.59; Br, 8.68. Calcd for $C_{37}H_{30}P_2SO_5IIr$: C, 45.9; H, 3.11; S, 3.31; I, 13.11. Found: C, 45.23; H, 3.22; S, 3.52; I, 12.70.

A saturated benzene solution of $Rh(P(C_6H_5)_3)_2COCl$ into which a slow stream of O_2 and SO_2 was bubbled for 12 hr upon evaporation gave a material whose ir spectrum showed sulfate bands ((KBr) 2075, 1285, 1156, 1167, 857, 888, 657 cm^{-1}) analogous to those of $Ir(P(C_6H_5)_3)_2(CO)(Cl)(SO_4)$, presumably $Rh(P(C_6H_5)_3)_2(CO)(Cl)(SO_4)$, but this material could not be separated from the starting material.

4. **Reaction of $Rh(P(C_6H_5)_3)_3(NO)$ with SO_2.**—Red solutions of $Rh(P(C_6H_5)_3)_3(NO)$ in benzene turned dark brown upon treatment with SO_2 but no stable products could be obtained from these solutions. Passing a stream of inert gas through the solution led to restoration of the red color and $Rh(P(C_6H_5)_3)_3(NO)$ could be recovered.

5. **Reaction of $Rh(P(C_6H_5)_3)_3(NO)$ with O_2 and $O_2 + SO_2$.**—Solutions of $Rh(P(C_6H_5)_3)_3(NO)$ in benzene or tetrahydrofuran discolored rapidly in air giving a brown precipitate whose ir spectrum had bands usually characteristic of $(C_6H_5)_3P{=}O$. However, if $Rh(P(C_6H_5)_3)_3(NO)$ was dssolved in benzene saturated with SO_2 at room temperature and then a stream of O_2 was passed into the solution, a green insoluble complex precipitated from the solution. This was removed by filtration and vacuum dried. *Anal.* Calcd for $Rh(P(C_6H_5)_3)_2(SO_4)(NO)$, $C_{36}H_{30}NP_2O_5Rh$: C, 57.4; H, 3.98; N, 4.26; S, 1.86. Found: C, 53.5; H, 3.96; N, 4.28; S, 1.81. Dissolving $Rh(P(C_6H_5)_3)_2(SO_4)(NO)$ in CH_2Cl_2 followed by adding benzene gave an ill-defined new material which was not isolated in pure form.

It was found that $Ir(P(C_6H_5)_3)_3(NO)$ exposed to O_2 as above gave a brown solid containing $(C_6H_5)_3P{=}O$ while exposure to SO_2 led to no reaction. A solution of $Ir(P(C_6H_5)_3)_3(NO)$ (75 mg) in 5 ml of CH_2Cl_2 was saturated with SO_2. A slow stream of O_2 was passed through this solution for 10 min. The product was precipitated by hexane addition as a beige powder. This material gave an ir spectrum very similar to that observed for the rhodium nitrosyl sulfate but consistently high S analyses were obtained. The ir spectrum in KBr gave ν(NO) 1612 (s) cm^{-1} and $\nu(SO_4)$ 1295 (m), 1155 (s), 872 (w), 855 (w), and 650 cm^{-1} (s). Recrystallization attempts gave intractable materials having ir spectra similar to those of materials obtained upon attempts to recrystallize the rhodium nitrosyl sulfate.

6. **Chloroperoxotris(triphenylphosphine)iridium.**—A saturated solution of $Ir(P(C_6H_5)_3)_3Cl$ in benzene was stirred in air 3 min or until the solution was deep yellow. Addition of CH_3OH gave a salmon-colored precipitate which was removed by filtration and then washed with methanol. This complex is somewhat air sensitive, decomposing to a blue substance and $P(C_6H_5)_3O$ in a few days when exposed to air. It is more stable if kept under vacuum. *Anal.* Calcd for $C_{54}H_{45}P_3ClO_2Ir$: C, 61.9; H, 4.30; Cl, 3.39; P, 8.6. Found: C, 61.6; H, 4.51; Cl, 3.31; P, 8.68. This reaction was also carried out with $^{18}O_2$ (92% enrichment).

Passage of a stream of CO through a solution of $Ir(P(C_6H_5)_3)_3ClO_2$ for 15 min led to no apparent reaction. A solution of $Ir(P(C_6H_5)_3)_3ClO_2$ in benzene, when placed under 60 psi of CO for 6 hr and then flash evaporated, did, however, give a mixture indicated by ir to contain $Ir(P(C_6H_5)_3)_2(CO)(Cl)(O_2)$, $Ir(P(C_6H_5)_3)_2(CO)(Cl)$, and $(C_6H_5)_3P{=}O$ among other substances.

7. **Reaction of $Ir(P(C_6H_5)_3)_3(Cl)(O_2)$ with SO_2.**—A solution of 20 mg of $Ir(P(C_6H_5)_3)_3(Cl)$ in 3 ml of benzene was exposed to air until it turned yellow; then 15 mg of $P(C_6H_5)_3$ was added. A slow stream of SO_2 was passed through the solution for 30 sec whereupon the solution became greenish yellow. The product was precipitated by hexane addition, removed by filtration, and vacuum dried. *Anal.* Calcd for $Ir(P(C_6H_5)_3)_3(Cl)(SO_4)$, $C_{54}H_{45}P_3ClSO_4Ir$: C, 58.4; H, 4.05; S, 2.88; Cl, 3.20. Calcd for $Ir(P(C_6H_5)_3)_2(Cl)(SO_4)$, $C_{36}H_{30}P_2ClSO_4Ir$: C, 50.8; H, 3.18; S, 3.78; Cl, 4.19. Found: C, 51.23; H, 3.88; S, 3.37; Cl, 31.73. The infrared spectrum in CsI showed sulfate bands: 1270 (s), 1155 (s), 900 (w), 655 (s), 555 cm^{-1} (m).

If the above procedure was carried out without addition of excess $P(C_6H_5)_3$ or if material obtained above was recrystallized in the absence of $P(C_6H_5)_3$, the resulting substance gave ir spectra resembling those obtained from reaction of $Ir(P(C_6H_5)_3)_2(Cl)(N_2)$ with $SO_2 + O_2$ (procedure 8). Passage of CO through a solution of material prepared with or without added $P(C_6H_5)_3$ resulted in immediate bleaching and high yields of $Ir(P(C_6H_5)_3)_2(CO)(Cl)(SO_4)$ could be isolated.

8. **Reaction of $Ir(P(C_6H_5)_3)_2(Cl)(N_2)$ and $Ir(P(C_6H_5)_3)_3(Cl)$ with O_2 and with $O_2 + SO_2$.**—A. A suspension of 20 mg of $Ir(P(C_6H_5)_3)_2(Cl)(N_2)$ in 5 ml of benzene was prepared in a Schlenk tube and SO_2 was admitted to the tube. A red solution resulted, presumably due to formation of $Ir(P(C_6H_5)_3)_2(Cl)(SO_2)_2$ (see text). Evaporation of the red solution or addition of hexane (which would reduce the solubility of SO_2 in the solution) led to formation of a yellow precipitate, presumed to be $((P(C_6H_5)_3)_2ClIr)_2SO_2$ ($\nu(SO_2)$ (KBr) 545 (s), 907 (w), 980 (vw), 1120 cm^{-1} (m). Solutions of the yellow solid in benzene were not red and did not turn red if the solution was saturated with SO_2. Solutions of the yellow solid in tetrahydrofuran under CO at room temperature were found after several days to contain $Ir(P(C_6H_5)_3)_2(CO)_2(Cl)$. Treatment of a freshly prepared red solution with a CO stream followed by evaporation gave as a green solid $Ir(P(C_6H_5)_3)_2(Cl)(SO_2)(CO)$, identified by its ir spectrum. Passage of a slow stream of O_2 through the red solution for 15 min gave a green solution from which a second yellow powder precipitated. This material gave ir bands appropriate for a sulfate: $\nu(SO_4)$ (KBr) 662 (s), 908 (m), 1155 (s), 1263 cm^{-1} (m). It decomposed upon attempts to recrystallize it. However, passage of CO through the green solution or passage of CO through solutions of the second yellow solid in benzene gave solutions containing a mixture of compounds of which the major component was identified by ir analysis as $Ir(P(C_6H_5)_3)_2(CO)(Cl)(SO_4)$. The first yellow solid, $(((C_6H_5)_3P)_2ClIr)_2SO_2$, did not react readily with O_2 in solution.

B. A solution of $Ir(P(C_6H_5)_3)_3(Cl)$ in benzene saturated with SO_2 at room temperature was stirred for 2 hr. Addition of hexane then led to precipitation of a yellow solid whose ir spectrum was identical with that of the supposed $(((C_6H_5)_3P)_2ClIr)_2SO_2$. The red color due to $Ir(P(C_6H_5)_3)_2(Cl)(SO_2)_2$ was not observed.

9. **Attempted Preparation of Chlorocarbonatocarbonylbis(triphenylphosphine)iridium.**—A suspension of 50 mg of $Ir(P(C_6H_5)_3)_2(Cl)(SO_2)_2$ in 10 ml of benzene was stirred under 56 psi of CO at 75° for 12 hr. The yellow solution was evaporated at reduced pressure. The products were identified as $Ir(P(C_6H_5)_3)_2(CO)(I)$, $Ir(P(C_6H_5)_3)_2(CO)_2(I)$, and some $(C_6H_5)_3PO$ by infrared spectroscopy.

Acknowledgments.—We gratefully acknowledge helpful discussion with Dr. S. J. Lapporte and thank Professor M. Kubota for communication of his results prior to publication. Donald Valentine thanks Princeton University for a one-semester leave of absence. This research was supported under the auspices of the National Institutes of Health, Air Pollution Division (Grant No. AP 00794-01); the National Science Foundation (Grant No. GP-9101), and the Petroleum Research Fund (Grant No. 3635-C3).

Contribution from the Department of Chemistry,
University of Hong Kong, Pokfulam Road, Hong Kong

Structural and Mechanistic Studies of Coordination Compounds. I. The Preparation and Aquation of *trans*-Chloronitro- and *trans*-Chlorocyano(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Cations

By K. S. Mok and C. K. Poon*

Received April 16, 1970

The preparation and characterization of *trans*-Co(cyclam)NO_2Cl^+ and *trans*-Co(cyclam)$CNCl^+$ cations are described. The assignment of geometric configuration is based on infrared spectroscopy. In dilute nitric acid solution, pH 2, these complexes, supplied as the nitrates, aquate with complete retention of configuration with the loss of about 60% (at 33.0°) and 90% (at 67.0°), respectively, of the coordinated chloride at equilibrium. The aquation kinetics of these two complex cations have been studied over a range of temperature, giving the following activation parameters: *trans*-Co(cyclam)NO_2Cl^+, $\Delta H^{\ddagger} = 20.6 \pm 0.2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -9 \pm 0.5$ cal deg^{-1} mol^{-1}; *trans*-Co(cyclam)$CNCl^+$, $\Delta H^{\ddagger} = 23.5 \pm 0.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = -9 \pm 1.5$ cal deg^{-1} mol^{-1}. The thermodynamic and kinetic stability of octahedral cobalt(III)–amine complexes have been discussed in terms of the nephelauxetic effect of various ligands on the central metal ion. A dissociative mechanism is assigned to the aquation of these complexes. An "internal SN1CB" mechanism has been proposed for the aquation of *trans*-Co(cyclam)$OHCl^+$.

Introduction

The interpretation of acid hydrolysis rate data of cobalt(III)–amine complexes in terms of the duality of reaction mechanism has been seriously questioned in recent years.[1,2] Lately, Langford suggested that all these reactions were essentially unimolecular and that the steric course arose from a duality of geometry of the five-coordinate intermediate.[3] In order to put this proposition into test, Poon and Tobe have started a program to examine the substitution reactions of complexes of the type *cis*- and *trans*-Co(cyclam)ACl^+ (where cyclam is 1,4,8,11-tetraazacyclotetradecane and A is a nonlabile ligand) and have reported the aquation of *cis*- and *trans*-Co(cyclam)Cl_2^+ and *trans*-Co(cyclam)$OHCl^+$.[4–7] Their results supported Langford's proposition. Tobe further pointed out that for these reactions a square-pyramidal intermediate was invariably associated with a lower entropy of activation whereas a trigonal-bipyramidal intermediate was associated with a higher entropy of activation.[8]

trans-Co(cyclam)NO_2Cl^+ and *trans*-Co(cyclam)$CNCl^+$, on one hand, resemble the pair *trans*-Co(cyclam)$OHCl^+$ and *trans*-Co(cyclam)Cl_2^+ in having a stereoretentive ligand, cyclam, while, on the other hand, they resemble the controversial pair *trans*-$Co(en)_2NO_2Cl^+$ and *trans*-$Co(en)_2CNCl^+$ in having π-accepting ligands NO_2^- and CN^-. It would, therefore, be desirable to study the reactions of these two complexes in order to examine the general validity of Langford's and Tobe's propositions.

Experimental Section

Preparation of the Compounds. 1,4,8,11-Tetraazacyclotetradecane.—This compound was prepared by the method of Bosnich, Poon, and Tobe.[4]

***trans*-Chloronitro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Chloride.**—The perchlorate salt of this cation described by Bosnich, Poon, and Tobe is insoluble in water.[9] The soluble chloride salt was prepared by a modification of their method. A concentrated aqueous solution (20 ml) of cobalt(II) chloride hexahydrate (5.0 mM) was added with stirring to an aqueous solution (50 ml) of cyclam (5.0 mM) and sodium nitrite (30 mM) and was bubbled through the solution for 0.5 hr. A strong aqueous solution (20 ml) of sodium tetraphenylboron (5.0 mM) was slowly added to the filtered solution to precipitate the light brown crystals of *trans*-$[NO_2Co(cyclam)O_2Co(cyclam)NO_2](B(C_6H_5)_4)_2$, which were filtered off, washed with water, and air dried. The peroxo-bridged compound was converted into the chloride salt by dissolving the solid in a minimum amount of dry acetone. Addition of an excess of a strong solution of lithium chloride in acetone immediately precipitated the peroxo-bridged compound as a dark brown viscous liquid. The supernatant acetone solution was poured off and the residue was washed twice with fresh acetone and ether. Concentrated hydrochloric acid (2 ml) was added to dissolve the viscous mass. To the filtered reddish solution, excess alcohol and ether were added to precipitate the pinkish red *trans*-[Co(cyclam)NO_2Cl]Cl which was recrystallized

---

* To whom correspondence should be addressed.

[1] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967.

[2] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965.

[3] C. H. Langford, *Inorg. Chem.*, **3**, 228 (1964).

[4] B. Bosnich, C. K. Poon, and M. L. Tobe, *ibid.*, **4**, 1102 (1965).

[5] C. K. Poon and M. L. Tobe, *Coord. Chem. Rev.*, **1**, 81 (1966).

[6] C. K. Poon and M. L. Tobe, *J. Chem. Soc. A*, 2069 (1967).

[7] C. K. Poon and M. L. Tobe, *ibid.*, *A*, 1549 (1968).

[8] M. L. Tobe, *Inorg. Chem.*, **7**, 1260 (1968).

[9] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **5**, 1514 (1966).