Electrophilic Behaviour of Nitrosyls: the Boedeker Reaction, the Reactions of Sulphite with Nitrosyls, and the Crystal and Molecular Structure of *cis*-Bis(2,2'-bipyridine)chloro(nitrosylsulphito)ruthenium †

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Similar adducts to that, $[Fe(CN)_5\{(NO)(SO_3)\}]^{4-}$, formed in the Boedeker reaction have been obtained by the reaction of SO_3^{2-} with *trans*-$[RuCl(py)_4(NO)]^{2+}$ (py = pyridine) or *cis*-$[RuX(bipy)_2(NO)]^{2+}$ (X = Cl or Br, bipy = 2,2'-bipyridine). These adducts, $[RuCl(py)_4\{N(O)SO_3\}]$ and *cis*-$[RuX(bipy)_2\{N(O)SO_3\}]$, are shown, principally by i.r. spectroscopy, to contain identical $[N(O)SO_3]^-$ ligands to $[Fe(CN)_5\{N(O)SO_3\}]^{4-}$. The structure of *cis*-$[RuCl(bipy)_2\{N(O)SO_3\}]$ has been determined by *X*-ray diffraction. It is best regarded as a ruthenium(II) complex containing the hitherto unknown ligand $[ONSO_3]^-$ which is N-co-ordinated to Ru^{II}. The ligand has a long (1.82 Å) and weak (force constant 137 N m^{-1}) N–S bond. The reversibility of the adduct formation is demonstrated. Crystal data for *cis*-$[RuCl(bipy)_2\{N(O)SO_3\}]$: orthorhombic, space group *Pbca*, *a* = 14.48(2), *b* = 19.49(2), *c* = 14.49(1) Å, final *R* = 0.063 for 290 variables and 1 370 observed reflections. The ruthenium is in a distorted octahedral environment.

In 1861 Boedeker[1] reported the formation of a deep red colour when sulphite, SO_3^{2-}, was added to $[Fe(CN)_5(NO)]^{2-}$ in aqueous solution. In retrospect this reaction appears to be the first example of the reaction of a co-ordinated ligand. Since Boedeker's first report the reaction has been investigated many times.[2] It has been established that the red colour is due to the reversible formation of a 1 : 1 adduct, $[Fe(CN)_5\{(NO)(SO_3)\}]^{4-}$ which decomposes in solution.[2,3] The final iron-containing product of the reaction of $[Fe(CN)_5(NO)]^{2-}$ with excess of SO_3^{2-} is $[Fe(CN)_5(SO_3)]^{5-}$,[4] but the fate of the nitrosyl group is not known (its loss as NO_2^- is the most probable reaction[2]). The structure of the 1 : 1 adduct has been the subject of considerable speculation. It was generally accepted that the association was between the nitrosyl ligand and SO_3^{2-}, but the mode of interaction was in dispute. Bonding between a sulphur or an oxygen atom of SO_3^{2-} and the nitrogen atom of the nitrosyl ligand has been proposed.[5] On the other hand an i.r. study of solid $Cs_4[Fe(CN)_5\{(NO)(SO_3)\}]$ favoured the attachment of sulphur from SO_3^{2-} to the oxygen atom of the nitrosyl.[6,7]

We were intrigued by the Boedeker reaction for several reasons. First, we felt that 120 years should have sufficed to answer the apparently simple problem of the nature of the red adduct. Secondly, $[Fe(CN)_5(NO)]^{2-}$ is one of a group of nitrosyls in which the nitrosyl ligand behaves as an electrophile.[8] We felt that the reaction of $[Fe(CN)_5(NO)]^{2-}$ with SO_3^{2-} was a further example of this general behaviour. The red adduct would be produced by attack of the least electronegative atom of SO_3^{2-}, namely the sulphur, at the nitrogen atom of the nitrosyl ligand in $[Fe(CN)_5(NO)]^{2-}$ thus giving $[Fe(CN)_5\{N(O)SO_3\}]^{4-}$. We wished to prove this postulate. Thirdly, if the postulate was correct the red adduct contained the ligand $[ONSO_3]^-$ in which the nitrogen atom was co-ordinated to iron(II). So far as we can ascertain neither salts of the $[ONSO_3]^-$ anion nor the parent acid have been prepared, although the anion has been implicated as an intermediate in the Raschig synthesis of hydroxylamine.[9] The Boedeker reaction would therefore represent an interesting example of the stabilisation of an apparently unstable anion by co-ordination to a metal.

The only definitive evidence for the structure of the red adduct would be provided by *X*-ray diffraction, and we initially attempted to obtain crystals of salts of $[Fe(CN)_5\{(NO)(SO_3)\}]^{4-}$. However, decomposition of the adduct prevented us from obtaining crystals suitable for diffraction. Pursuing our assumption that the reaction between $[Fe(CN)_5(NO)]^{2-}$ and SO_3^{2-} was an example of the electrophilic behaviour of nitrosyls we turned to other nitrosyl complexes showing such behaviour. Described here are the reactions of SO_3^{2-} with some nitrosyls, the isolation of three adducts of the type $[ML_5\{(NO)(SO_3)\}]$, the crystal and molecular structure of one of them, *cis*-$[RuCl(bipy)_2\{N(O)SO_3\}]$ (bipy = 2,2'-bipyridine) [showing that the ligand has the predicted $N(O)SO_3$ geometry], some reactions of the adducts, and convincing evidence that all of the adducts, including that produced in the Boedeker reaction, contain the same $M\{N(O)SO_3\}$ moiety. The structure of $M\{N(O)SO_3\}$ is also discussed.

Results and Discussion

Reactions of Sulphite with Nitrosyls.—Attempts to obtain usable crystals of $Cs_4[Fe(CN)_5\{(NO)(SO_3)\}]$, prepared by the literature method,[6] were not successful. We therefore turned to $[Ru(NH_3)_5(NO)]^{3+}$ which has been shown previously to behave as an electrophile.[8,10,11] Addition of OH^- to an aqueous solution of a mixture of $[Ru(NH_3)_5(NO)]^{3+}$ and excess of HSO_3^- gave at low pH $[Ru(NH_2)(NH_3)_4(NO)]^{2+}$ and at higher pH mainly $[Ru(NH_3)_5(NO_2)]^+$ with small quantities of $[Ru(NH_3)_5(N_2)]^{2+}$ and $[Ru(OH)(NH_3)_4(NO)]^{2+}$. These are the products of the reaction between $[Ru(NH_3)_5(NO)]^{3+}$ and OH^-.[10,11] We conclude that SO_3^{2-} acts as a simple Brønsted base towards $[Ru(NH_3)_5(NO)]^{3+}$ in aqueous solution. Similar behaviour has been observed for NH_3 and N_3^-.[8,11] Only nucleophiles powerful enough to compete with OH^- or which rapidly and irreversibly attack $[Ru(NH_3)_5(NO)]^{3+}$ are capable of reaction; SO_3^{2-} is in neither category.

Addition of excess of SO_3^{2-} to orange *trans*-$[RuCl(py)_4(NO)]^{2+}$ (py = pyridine) (which has recently been shown to

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† *Supplementary data available* (No. SUP 23705, 29 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles, least-squares planes, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

behave as an electrophile[12]) gave a 1 : 1, dark green, diamagnetic adduct [RuCl(py)$_4${(NO)(SO$_3$)}] in rather low (25%) yield. There was no reaction between *trans*-[RuCl(py)$_4$(NO)]$^{2+}$ and H_2SO_3. The low yield of [RuCl(py)$_4${(NO)(SO$_3$)}] is presumed to be due to steric reasons; the pyridine ligands which are arranged in a cogwheel fashion[13] resist approach of SO_3^{2-} and its bonding to the RuNO unit. The equilibrium between *trans*-[RuCl(py)$_4$(NO)]$^{2+}$ and [RuCl(py)$_4${N(O)SO$_3$}] favours the former. The adduct was insoluble in water, alcohol, and acetone and turned rapidly brown in solvents such as chloroform in which it was sparingly soluble. Therefore we have no direct proof of the stereochemistry about the ruthenium. The starting complex [RuCl(py)$_4$(NO)]$^{2+}$ is known to have the *trans* geometry,[13] and [RuCl(py)$_4${N(O)SO$_3$}] gave *trans* products on reaction (see below). Hence we assign it the *trans* stereochemistry as well.

Addition of either H_2SO_3 or Na_2SO_3 to an orange aqueous solution of *cis*-[RuX(bipy)$_2$(NO)]$^{2+}$ (X = Cl or Br), which are known from the work of Meyer and co-workers to behave as electrophiles,[8,14–17] gave an immediate colour change to green-black and quite rapid precipitation of the black crystalline 1 : 1 diamagnetic adduct in 75% yield. Crystals of the chloro-complex were subjected to *X*-ray diffraction and shown to be *cis*-[RuCl(bipy)$_2${N(O)SO$_3$}]. The much higher yield of the adduct as compared to that in the preparation of *trans*-[RuCl(py)$_4${N(O)SO$_3$}] is probably because the *cis* arrangement of the bipyridine ligands and their rigid positioning allows an easier approach of the SO_3^{2-} nucleophile. Despite this the complex is rather sterically crowded, as is shown by the structural investigation. Judging by their i.r. spectra, *cis*-[RuX(bipy)$_2$(NO)]$^{2+}$ [ν(NO) 1 931 cm^{-1} for X = Cl, 1 930 cm^{-1} for X = Br[14]] are slightly better electrophiles than *trans*-[RuCl(py)$_4$(NO)]$^{2+}$ [ν(NO) 1 910 cm^{-1} [12]]. For this reason as well as the steric one the equilibrium between the parent nitrosyl and the sulphite adduct will favour the adduct complex for [RuX(bipy)$_2$(NO)]$^{2+}$ as compared to [RuCl(py)$_4$(NO)]$^{2+}$. This is also shown by the fact that *cis*-[RuX(bipy)$_2$(NO)]$^{2+}$ reacted with both SO_3^{2-} and H_2SO_3, whereas *trans*-[RuCl(py)$_4$(NO)]$^{2+}$ only reacted with SO_3^{2-}.

Identity Relationship between the Adducts.—Since definitive structural evidence for the nature of the Boedeker adduct [Fe(CN)$_5${(NO)(SO$_3$)}]$^{4-}$ is not obtainable it is necessary to establish beyond doubt that the Fe{(NO)(SO$_3$)} moiety has the same structure as Ru{(NO)(SO$_3$)} in the three adducts which we have obtained in this work: *trans*-[RuCl(py)$_4${(NO)(SO$_3$)}], *cis*-[RuBr(bipy)$_2${(NO)(SO$_3$)}], and most importantly *cis*-[RuCl(bipy)$_2${N(O)SO$_3$)}] for which we have precise structural data. We also wish to establish the structural identity of all the adducts as [ML$_5${N(O)SO$_3$}]$^{n+}$.

All the adducts are formed reversibly and are 1 : 1 as shown by microanalysis (see ref. 6 for analytical data and physical properties of Cs$_4$[Fe(CN)$_5${(NO)(SO$_3$)}]). There is a reduction of two units of charge on each of the complexes when the adduct is formed from the parent nitrosyl and sulphite; thus all the complexes are adducts of SO_3^{2-} not HSO_3^- or H_2SO_3. The complexes are diamagnetic. Considering the starting nitrosyls as containing *formally* NO$^+$ and Fe^{II} or Ru^{II}, the diamagnetism shows that the complexes *formally* contain Fe^{II} or Ru^{II} and [(NO)(SO$_3$)]$^-$. The [Fe(CN)$_5${(NO)(SO$_3$)}]$^{4-}$ complex is characterised by an intense absorption maximum at 475 nm in the electronic absorption spectrum (the origin of the Boedeker red colour). The ruthenium complexes were insoluble in solvents which did not react with them and it was therefore possible to measure only reflectance spectra. Figure 1 shows these spectra. It is seen that all the adduct complexes have an absorption maximum in the 450—475 nm region, although the spectra of the ruthenium complexes are complicated by an absorption at higher wavelength. This is probably due to the pyridine ligands since the parent nitrosyl complexes absorb at higher wavelengths than [Fe(CN)$_5$(NO)]$^{2-}$.

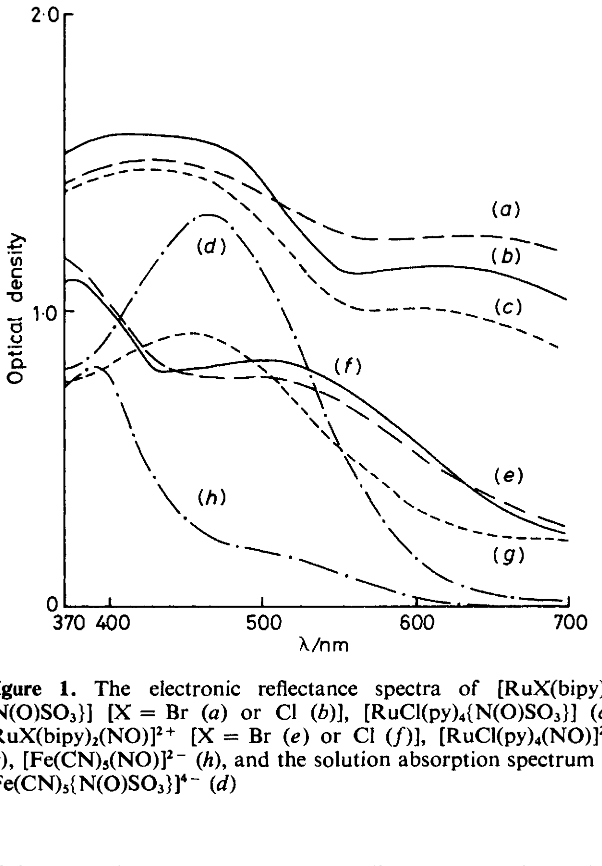


Figure 1. The electronic reflectance spectra of [RuX(bipy)$_2${N(O)SO$_3$}] [X = Br (*a*) or Cl (*b*)], [RuCl(py)$_4${N(O)SO$_3$}] (*c*), [RuX(bipy)$_2$(NO)]$^{2+}$ [X = Br (*e*) or Cl (*f*)], [RuCl(py)$_4$(NO)]$^{2+}$ (*g*), [Fe(CN)$_5$(NO)]$^{2-}$ (*h*), and the solution absorption spectrum of [Fe(CN)$_5${N(O)SO$_3$}]$^{4-}$ (*d*)

The most convincing evidence that all of the adduct complexes have the same structure for the M{(NO)(SO$_3$)} moiety is provided by the i.r. spectra. Table 1 lists the absorption bands, their relative intensities, and assignments confirmed by a normal-co-ordinate analysis of M{N(O)SO$_3$} with the structure of *cis*-[RuCl(bipy)$_2${N(O)SO$_3$}]. Note that of the 15 normal vibrations of M{N(O)SO$_3$} ten have been identified for each of the adduct complexes and there is an extremely close correspondence in the frequencies and relative intensities of the ten i.r. bands. The remaining five bands are expected to occur at low frequency (<300 cm^{-1}).

From the accumulated evidence we conclude that the structure of the M{(NO)(SO$_3$)} moiety is the same in all the adduct complexes. Therefore the structure of *cis*-[RuCl(bipy)$_2${N(O)SO$_3$}] described below proves that the Boedeker and all the other adducts may be described as [ML$_5${N(O)SO$_3$}]$^{n-}$ complexes. These are formed by nucleophilic attack of the sulphur atom of SO_3^{2-} at the nitrogen atom of co-ordinated NO. Such a reaction is in complete accord with the kinetic data of Andrade and Swinehart[7] for the Boedeker reaction, although these authors assumed bonding of sulphur to the oxygen of the NO ligand.

Reactions of the [RuL$_5${N(O)SO$_3$}] *Complexes.*—In aqueous acid (HCl) solution both *cis*-[RuCl(bipy)$_2${N(O)SO$_3$}] and *trans*-[RuCl(py)$_4${N(O)SO$_3$}] reverted essentially quantitatively to the parent nitrosyls *cis*-[RuCl(bipy)$_2$(NO)]$^{2+}$ and *trans*-[RuCl(py)$_4$(NO)]$^{2+}$. Hence formation of the Ru{N(O)SO$_3$} adduct is reversible, as is also the case for the Boedeker reaction. However, in neutral solution *cis*-[RuCl(bipy)$_2${N(O)SO$_3$}] gave *cis*-[RuCl(bipy)$_2$(NO)]$^{2+}$ in only 50% yield,

Table 1. Vibrational wavenumbers (cm^{-1}) and assignments for $[ML_5\{N(O)SO_3\}]^{n-}$ complexes; calculated values are given in parentheses

$Cs_4[Fe(CN)_5\{^{14}N(O)SO_3\}]$ [a,b]	*trans*-$[RuCl(py)_4\{^{14}N(O)SO_3\}]$ [b]	*trans*-$[RuCl(py)_4\{^{15}N(O)SO_3\}]$ [b]	*cis*-$[RuBr(bipy)_2\{^{14}N(O)SO_3\}]$ [b]	*cis*-$[RuCl(bipy)_2\{^{14}N(O)SO_3\}]$ [b,c]	*cis*-$[RuCl(bipy)_2\{^{15}N(O)SO_3\}]$ [b]	Assignment
1 357s (1 354)	1 346s	1 325s	1 372s	1 370s (1 370)	1 352s (1 347)	ν(N–O)
1 252s (1 244)	1 273s (sh)	1 275s (sh)	1 270s (sh)	1 267s (sh) (1 263)	1 267s (sh) (1 267)	ν_{asym}(S–O)
1 229s (1 240)	1 258s	1 255s	1 255s	1 250s (1 256)	1 250s (1 251)	ν_{sym}(S–O)
1 041s (1 040)	1 031s	1 030s	1 040s	1 038s (1 040)	1 038s (1 040)	ν_{sym}(S–O)
758w (758)	770	758 [d]	775 [e]	775 [e] (781)	765 [e] (762)	δ(O–N–S)
621s (622, 619)	604m [f]	590s	605s [f]	612 [f] (610)	607	δ_{asym}(O–S–O)
	598m [f]		602s [f]	608 [f] (610)	(610, 609)	δ_{sym}(O–S–O)
570w						
547 (sh)						
542m (543)	537	528m	533m	541m (532)	535m (531)	$\rho_{sym}(SO_3)$ def.
	518	507w	512w	516w	513w	
(444, 405) [h]				420w (427, 422)	(418, 417)	$\rho(N{-}SO_3)$ wag.

[a] Observed frequencies taken from ref. 3. [b] s = Strong, m = medium, w = weak, sh = shoulder. [c] For the $Ru\{^{14}N(O)SO_3\}$ group five low-frequency bands were calculated: 268, 220, 199, 147, and 96 cm^{-1}. [d] A pyridine absorption occurs at 760 cm^{-1} and obscures this region. [e] A bipyridine absorption occurs in this region; by comparison with other $[Ru(bipy)_2XY]^{n+}$ complexes it is possible to distinguish the band due to the $[ONSO_3]^-$ ligand, but the exact frequency and intensity cannot be judged with certainty. [f] These bands appear as a poorly resolved doublet. [g] We are unable to assign this band either to the $Fe\{N(O)SO_3\}$ or the $Fe(CN)_5$ fragment. [h] Ref. 3 does not report an absorption band below 542 cm^{-1}.

and the reactions were not always reproducible; *trans*-$[RuCl(py)_4\{N(O)SO_3\}]$ gave $[Ru(OH)(py)_4(NO)]^{2+}$, but again the yield was low. The filtrates remaining after preparing the ruthenium adduct complexes were also investigated. They contained both nitrosyl and nitro-derivatives {*e.g.* $[Ru(OH)(py)_4(NO)]^{2+}$, $[RuCl(bipy)_2(NO)]^{2+}$, or $[RuCl(bipy)_2(NO_2)]$}. There was no evidence of complexes in which the Ru–N bond had been broken. This is in contrast to $[Fe(CN)_5\{N(O)SO_3\}]^{4-}$, for which $[Fe(CN)_5X]^{n-}$ substitution products have been observed,[2,4] and indicates that the Ru–N bond is stronger than Fe–N in these complexes. With aqueous NH_3, *cis*-$[RuCl(bipy)_2\{N(O)SO_3\}]$ gave $[Ru(NH_3)(bipy)_2(NO_2)]^+$; the latter was also obtained by the reaction between *cis*-$[RuCl(bipy)_2(NO)]^{2+}$ [14] and aqueous NH_3. We believe the reaction of *cis*-$[RuCl(bipy)_2\{N(O)SO_3\}]$ with NH_3 proceeds through the sequence (1)—(3). Addition of dilute aqueous HCl converted $[Ru(NH_3)(bipy)_2(NO_2)]^+$ into $[Ru(NH_3)(bipy)_2(NO)]^{3+}$.

$$[RuCl(bipy)_2\{N(O)SO_3\}] \rightleftharpoons [RuCl(bipy)_2(NO)]^{2+} + SO_3^{2-} \quad (1)$$

$$[RuCl(bipy)_2(NO)]^{2+} + 2OH^- \rightleftharpoons [RuCl(bipy)_2(NO_2)] + H_2O \quad (2)$$

$$[RuCl(bipy)_2(NO_2)] + NH_3 \longrightarrow [Ru(NH_3)(bipy)_2(NO_2)]^+ + Cl^- \quad (3)$$

The $M\{N(O)SO_3\}$ *Moiety.*—As outlined above, the physical properties of the complexes and the reactions which produce them suggest tha tthe $M\{N(O)SO_3\}$ moiety is best regarded as co-ordination of the nitrogen atom of the $[ONSO_3]^-$ ligand to a metal(II) complex. Neither the anion $[ONSO_3]^-$ nor the parent acid nor any complexes of these has been described previously, although kinetic data indicate that $[ONSO_3]^-$ is an intermediate in the Raschig synthesis of hydroxylamine (NH_2OH) from NO_2^- and HSO_3^-.[9] The radical dianion $[ONSO_3]^{2-}$ has been suggested as an intermediate in the formation of $[ONN(O)SO_3]^{2-}$.[18,19] There are two ions which are closely related to $[ONSO_3]^-$: the ion of the well known Fremy's salt, $[ON(SO_3)_2]^{2-}$,[20,21] and its diamagnetic form $[ON(SO_3)_2]^{3-}$.[22] The hydroxylamine derivative $[HON(H)SO_3]^-$ also exists.[23]

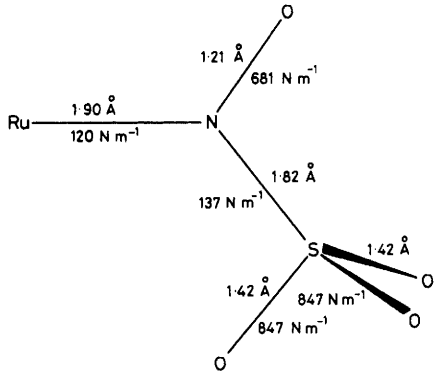


Figure 2. Distances and force constants in the $Ru\{N(O)SO_3\}$ moiety. In calculating the force constants, an idealised geometry having a plane of symmetry through RuN(1)O(1)SO(2) was assumed

Figure 2 shows the structural details of the $Ru\{N(O)SO_3\}$ moiety, with calculated force constants and observed distances. A complete list of force constants is given in Table 2 and of distances and angles in Tables 3 and 4. The unit RuNO(1)S is essentially planar with the SO_3 group rotated about the N–S bond such that the O(1)NSO(2) torsion angle

Table 2. Force constants for the Ru{N(O)SO_3} unit

Co-ordinate	Force constant ($N\ m^{-1}$)
N–O stretch	681 [a]
N–S stretch	137 [b,c]
S–O stretch	847 [d]
O–N–S bend	89.1
N–S–O bend	36.4
O–S–O bend	96.6 [e]
Ru–N–S bend	66.0
S–O/S–O′ interaction	36.1
Ru–N stretch	120 [f]
O–N–S–O torsion	5 [g]
Ru–N–S–O torsion	5 [g]
N(O,Ru,S) out-of-plane wag	5 [g]

[a] 1 040 N m^{-1} in NO_2,[31] 580 N m^{-1} in NO_2^-,[33] and 841 N m^{-1} in NO_3^- (C. W. F. T. Pistorius, *J. Chem. Phys.*, 1958, **29**, 1174). [b] 220 N m^{-1} in $^+H_3NSO_3^-$.[29] [c] The Urey-Bradley force constants in the cited work are expected to be lower than the valency-field constants obtained in the present investigation. [d] 750 N m^{-1} in $^+H_3NSO_3^-$ (see footnote *c*),[29] 1 023 N m^{-1} in SO_3,[27] 550 N m^{-1} in SO_3^{2-} (J. C. Evans and H. J. Bernstein, *Can. J. Chem.*, 1955, **33**, 1270), and 690 N m^{-1} (calc.) in SO_4^{2-}. [e] 115 N m^{-1} (calc.) in SO_4^{2-}. [f] Held constant, see text. [g] Estimated and held constant.

Table 3. Important bond distances (Å) in *cis*-[RuCl(bipy)$_2${N(O)-SO_3}]

Ru–Cl	2.379(5)	N(1)–S	1.820(15)
Ru–N(A)	2.082(12)	N(1)–O(1)	1.208(17)
Ru–N(A′)	2.122(13)	S–O(2)	1.423(12)
Ru–N(B)	2.041(12)	S–O(3)	1.420(13)
Ru–N(B′)	2.058(13)	S–O(4)	1.418(13)
Ru–N(1)	1.904(14)		

Table 4. Important bond angles (°) in *cis*-[RuCl(bipy)$_2${N(O)-SO_3}]

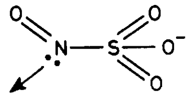
N(1)–Ru–Cl	90.1(4)	Ru–N(1)–O(1)	123.8(12)
N(1)–Ru–N(A)	96.1(5)	Ru–N(1)–S	127.9(7)
N(1)–Ru–N(B)	95.9(5)	O(1)–N(1)–S	108.0(11)
N(1)–Ru–N(B′)	95.5(5)	N(1)–S–O(2)	103.3(7)
Cl–Ru–N(A)	86.9(4)	N(1)–S–O(3)	104.9(7)
Cl–Ru–N(A′)	86.1(4)	N(1)–S–O(4)	102.3(7)
Cl–Ru–N(B′)	94.6(4)	O(2)–S–O(3)	114.2(8)
N(A)–Ru–N(A′)	76.5(5)	O(2)–S–O(4)	113.4(8)
N(A)–Ru–N(B)	97.1(5)	O(3)–S–O(4)	116.5(8)
N(A′)–Ru–N(B)	88.6(5)		
N(A′)–Ru–N(B′)	92.0(5)		
N(B)–Ru–N(B′)	80.1(5)		

Table 5. Equation * of the plane RuN(1)O(1)S of Ru{N(O)SO_3} with distances (Å) from the plane in square brackets

$$0.207X + 0.425Y + 0.881Z = 8.773$$

[Ru −0.012, N(1) +0.038, O(1) −0.015, S(1) −0.011, O(2) −0.425, O(3) −0.886, O(4) +1.386]

* *X*, *Y*, and *Z* are orthogonal co-ordinates (Å) related to the crystallographic axes by $X = ax$, $Y = by$, and $Z = cz$.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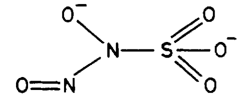
(II)

is 164.4° [the oxygen atoms O(1) and O(2) are *trans* to one another] (see Table 5). This *trans* arrangement is determined primarily by steric factors; a *cis* geometry would give an O(1)–O(2) distance of approximately 2.02 Å, which is very much shorter than the van der Waals diameter of oxygen (3.0 Å). There is therefore a very high steric barrier to free rotation of the SO_3 group about the N–S bond. The three OSO angles are very similar averaging 114.7(8)°, and the three NSO angles are likewise similar, averaging 103.5(7)°. The longer S–N distance [1.82(1) Å] compared to the S–O distances [1.42(1) Å] allows the NSO angle to be reduced compared to the OSO angle in order to minimise repulsion of the electron pairs.

The average S–O distance [1.42(1) Å] is at the shorter end of the distances generally observed in related SO_3^{2-} compounds (1.41—1.51 Å with an unweighted average of 1.44 Å [18–26]) and the stretching force constant (847 N m^{-1}) is also rather high (although not as high as the 1 023 N m^{-1} for SO_3[27] for which a full S=O double bond is expected). On the other hand the N–S distance [1.82(1) Å] is one of the longest yet observed, even longer than the 1.76(2) Å in $^+H_3NSO_3^-$,[28] although shorter than the 1.844(2) Å found in $(CH_3)_3N(SO_3)$.[24] The force constant (137 N m^{-1}) is also less than that calculated [29] for $^+H_3NSO_3^-$ (220 N m^{-1}). The very long N–S distance may be caused by steric repulsion of the oxygen atoms; the O(1)–O(3) non-bonding distance is 2.74 Å and O(1)–O(4) 2.96 Å. The N–O(1) distance [1.21(2) Å] and N–O force constant (681 N m^{-1}) lie between those of NO_2 and NO_2^- [1.188(4) Å,[30] 1 040 N m^{-1};[31] and 1.24(1) Å,[32] 580 N m^{-1} [33]] respectively. The co-ordination about the nitrogen atom is planar [RuNO 124(1), RuNS 127.9(7), and ONS 108(1)°; sum 359.9°].

The structural parameters for the Ru{N(O)SO_3} group are similar to those in both the ion of Fremy's salt, $[ON(SO_3)_2]^{2-}$ [ONS(1) = ONS(2) 120(2), SNS 118(2)°, sum = 358°;[21] N–O 1.28(4)[21] or 1.27(1)[20] Å; S–O 1.43(1) Å [20,21]] and to those in $[O_3SN(O)NO]^{2-}$ [ONS 118(2), SNN 117(2), NNO 125(2), sum = 360°; N–O 1.29(2) Å; S–O 1.44(1) Å].[19] The N–S distances in these ions are however shorter than the 1.82(1) Å found for *cis*-[RuCl(bipy)$_2${N(O)SO_3}]: in Fremy's salt N–S is 1.66(3)[21] or 1.73(1)[20] Å; in $[O_3SN(O)NO]^{2-}$ N–S is 1.79(1) Å.[19] In contrast $[ON(SO_3)_2]^{3-}$ has a pyramidal geometry about the N atom [ONS(1) = ONS(2) 107.7(1), SNS 114.4(1)°; sum = 329.8°], a much longer N–O distance [1.415(5) Å], longer S–O distances [average 1.455(3) Å], but a similar N–S distance [1.727(2) Å] to Fremy's salt.[22]

The distances, angles, and force constants within the Ru{N(O)SO_3} unit clearly show that in valence-bond terms the overwhelming contribution to the bonding in the ligand is provided by structure (I); $[O_3SN(O)NO]^{2-}$ has a similar structure (II). The $[ON(SO_3)_2]^-$ anion would be the exact analogue of these. It appears to be unknown. The ion of Fremy's salt, $[ON(SO_3)_2]^{2-}$, has an extra electron primarily localised in a π^*(NO) orbital; the two extra electrons of $[ON(SO_3)_2]^{3-}$ are effectively localised on the nitrogen atom giving a pyramidal geometry.

The population of the π^*(NO) orbital by one electron in Fremy's salt will be paralleled in the Ru{N(O)SO_3} case by population of the same π^*(NO) orbital by back donation of electrons from the ruthenium. That such π bonding occurs is indicated by the Ru–N(1) distance of 1.90(1) Å, which is considerably shorter than the average Ru–N distance to the bipyridine ligands [2.08(1) Å]. In $[Ru(NH_3)_5(NO_2)]^+$ the Ru–NH_3 distances average 2.141(5) Å and the Ru–NO_2 distance is 1.906(5) Å.[34] In $[\{Ru(bipy)_2(NO_2)\}_2O][ClO_4]_2$ the

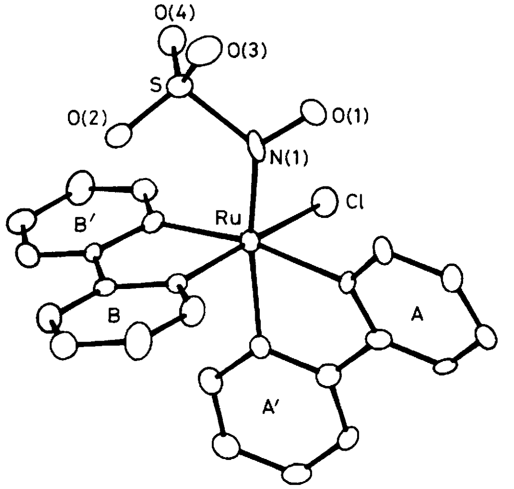

Figure 3. The geometry of the *cis*-$[RuCl(bipy)_2\{N(O)SO_3\}]$ molecule showing the numbering scheme used in the text and Tables 3—5

$Ru-NO_2$ distance is 2.05(1) Å and the Ru-bipy distances average 2.08 Å.[35] Ruthenium(II)-ammine distances are generally close to 2.13 Å, and Ru^{II}-bipy (or related ligands) close to 2.08 Å.[34-40] Very strongly π-bonded ligands such as NO have Ru–N distances close to 1.75 Å.[40-46] Hence the Ru–N π bonding in *cis*-$[RuCl(bipy)_2\{N(O)SO_3\}]$ is comparable to that for NO_2, but less than that of NO.

In calculating the force constants and frequencies listed in Tables 1 and 2 a difficulty arose with the Ru–N stretching constant. As the crystallographic investigation shows, there is multiple bonding between Ru and N, but its magnitude is difficult to assess. There are no well determined Ru–N force constants in the literature. Finally, the frequency of this vibration will be low, and therefore not well determined by the available data. The solution adopted was an empirical one. Initially a value of 115 N m^{-1} was assumed for the Ru–N stretching constant, and with this fixed the constants for the N, O, and S interactions listed in Table 2 were varied to obtain a fit of the frequencies. The Ru–N constant was then altered and in some cases allowed to vary freely with the other constants. Results were judged on the basis of the fit of the frequencies and the values of the force constants when compared to literature values. The set of frequencies and force constants calculated in Tables 1 and 2 were obtained using a fixed Ru–N stretching constant of 120 N m^{-1}. In this model there is no observable Ru–N stretching mode; the lower frequencies include contributions from Ru–N stretching and several bendings. The frequencies and force constants of the $\{N(O)SO_3\}$ group are of course affected by the Ru–N constant, but this does not affect the assignment of the i.r. bands of the $M\{N(O)SO_3\}$ group, nor the arguments about the identity of the structure of this group for all the adducts. The force constants for the $Fe\{N(O)SO_3\}$ group were essentially identical to those of $Ru\{N(O)SO_3\}$.

Structure of cis-$[RuCl(bipy)_2\{N(O)SO_3\}]$.—The crystal contains closely packed molecular units of the complex, there being rather short (1.55 Å) intermolecular distances between the (calculated) positions of the hydrogen atoms in the five positions on rings A and A′ of adjacent molecules. As obtained by the procedure described in the Experimental section, *cis*-$[RuCl(bipy)_2\{N(O)SO_3\}]$ always crystallised with one water molecule per formula unit, as judged by both microanalytical and i.r. data. However, there was no evidence in Fourier or in the final difference syntheses for the presence of water of crystallisation in the crystal used for the diffraction experiment.

The co-ordination about the ruthenium is basically octahedral (see Figure 3). The main deviations from angles of 90° are caused by the small bite-angle of the bipyridine ligand; the N(A)RuN(A′) angle is 76.5(5)°, and N(B)RuN(B′) is 80.1(5)°. The average, 78.3(5)°, is identical to that in other ruthenium complexes containing bipyridine (78.2°).[36-39] The average Ru–N distance of 2.08(1) Å is also the same as found elsewhere. The bipyridine ligands are not planar but are bowed about the 2,2′ ring fusion, the planes through rings A and A′ intersecting at an angle of 17.6° and through rings B and B′ at 5.7°. Such bowing was also observed in $[Ru(OH)(bipy)_2(H_2O)][ClO_4]_2$.[39] In addition the bipyridine ligands are bent away from the $[N(O)SO_3]^-$ ligand. The fact that the Cl^- is not bent away suggests that steric repulsion between the $[N(O)SO_3]^-$ and bipyridine ligands is responsible for the large N(1)RuN(bipy) angles, which average 95.8°. The Ru–Cl distance [2.379(5) Å] is in the range (2.36—2.39 Å) previously observed.[37,41-46]

Experimental

The starting materials $[Ru(NH_3)_5(NO)]Cl_3 \cdot H_2O$ [10] and $[RuCl(py)_4(NO)][ClO_4]_2$ were prepared by literature methods;[12] $[RuCl_2(bipy)_2]Cl$ and $[Ru(NO_2)_2(bipy)_2]$ were prepared as described below and the latter was converted into $[RuX(bipy)_2(NO)][ClO_4]_2$ (X = Cl or Br) by the method of Godwin and Meyer.[14,16] All other chemicals were reagent grade.

Bis(2,2′-bipyridine)dichlororuthenium Chloride Dihydrate, $[RuCl_2(bipy)_2]Cl \cdot 2H_2O$.—Ruthenium trichloride (Engelhardt Industries) (0.5 g) was activated by refluxing in a mixture of water (20 cm^3), HCl (12 mol dm^{-3}, 20 cm^3), and ethanol (20 cm^3) for 2 h. The activated solution was evaporated to dryness in a porcelain dish on a steam-bath. The residue was dissolved in a mixture of aqueous hydrochloric acid (12 mol dm^{-3}, 1 cm^3) and water (10 cm^3), transferred to a small beaker, and formic acid (5 cm^3) was added. The resultant solution was heated (uncovered) at 80—85 °C until it became green (*ca.* 1 h). To the still hot deep green solution was added a solution of 2,2′-bipyridine (0.75 g) in a mixture of acetone (20 cm^3) and water (20 cm^3). The resultant solution was heated on a water-bath for 10 min, HCl (12 mol dm^{-3}, 5 cm^3) added, and the volume reduced to *ca.* 15 cm^3. On standing overnight at room temperature brown crystals formed. These were collected by filtration, washed with acetone and diethyl ether, and air dried. The crude product was recrystallised from hydrochloric acid (3 mol dm^{-3}) as red crystals. Yield 1.2 g (55%) (based on $RuCl_3 \cdot 3H_2O$) [Found: C, 43.4; H, 3.6; Cl, 19.0; N, 10.1; Ru, 18.4; H_2O (Karl Fischer method), 6.5%. Calc. for $C_{20}H_{20}Cl_3N_4O_2Ru$: C, 43.2; H, 3.6; Cl, 19.2; N, 10.1; Ru, 18.1; H_2O, 6.5%]; effective magnetic moment 1.82×10^{-23} J T^{-1} (291 K) [lit.,[47] 1.87×10^{-23} J T^{-1} (297 K)]. Electronic spectrum (CH_3OH solution): $\lambda_{max.}$ 378 nm ($\varepsilon = 5.4 \times 10^3$ dm^3 mol^{-1} cm^{-1}); lit., 379 ($\varepsilon = 5.9 \times 10^3$) in CH_3OH,[48] 379 nm ($\varepsilon = 5.1 \times 10^3$ dm^3 mol^{-1} cm^{-1}) in CH_2Cl_2.[49]

cis-*Bis(2,2′-bipyridine)dinitroruthenium Hydrate*, *cis*-$[Ru(NO_2)_2(bipy)_2] \cdot H_2O$.—The salt $[RuCl_2(bipy)_2]Cl \cdot 2H_2O$ (0.2 g) was dissolved as rapidly as possible in hot water (100 cm^3), the solution filtered, and $NaNO_2$ (0.1 g) added to the reddish brown filtrate. The mixture was warmed (75 °C) and the colour changed to pale brown. On concentrating the solution by heating, red crystals of $[Ru(NO_2)_2(bipy)_2]\cdot H_2O$ appeared. These were collected by filtration, washed with water, ethanol, and diethyl ether, and dried *in vacuo*. Yield 0.10 g, 50%. The product had identical chemical and physical properties to those described by Godwin and Meyer.[14,16]

cis-*Chloro- and Bromo-bis*(2,2′-*bipyridine*)(*nitrosylsulphito*)-*ruthenium Hydrate*, *cis*-$[RuX(bipy)_2\{N(O)SO_3\}]\cdot H_2O$ (X = Cl *or* Br).—To a solution of $[RuCl(bipy)_2(NO)][ClO_4]_2$ (0.1 g) in a mixture of ethanol and water (1 : 1, 10 cm^3) was added H_2SO_3 (6% aqueous solution, 2 cm^3) dropwise. The colour of the solution changed immediately from orange to green-black and after *ca.* 5 min the black product began to crystallise on the walls of the flask. The flask was stoppered and set aside overnight at room temperature before collecting the $[RuCl(bipy)_2\{N(O)SO_3\}]\cdot H_2O$ product by filtration. The crystals were washed with water, ethanol, and diethyl ether, and dried *in vacuo*. Yield 0.065 g (75%) (Found: C, 41.7; H, 3.0; Cl, 6.4; N, 12.0; S, 5.5. Calc. for $C_{20}H_{18}ClN_5O_5RuS$: C, 41.6; H, 3.1; Cl, 6.1; N, 12.1; S, 5.6%).

The bromo-complex was prepared exactly analogously from $[RuBr(bipy)_2(NO)][ClO_4]_2$ in 75% yield (Found: C, 39.0; H, 2.7; N, 11.3. Calc. for $C_{20}H_{18}BrN_5O_5RuS$: C, 38.6; H, 2.9; N, 11.3%).

Reactions of cis-$[RuCl(bipy)_2\{N(O)SO_3\}]\cdot H_2O$.—(*a*) *With water: formation of* cis-*bis*(2,2′-*bipyridine*)*chloronitrosylruthenium bis*(*hexafluorophosphate*), *cis*-$[RuCl(bipy)_2(NO)][PF_6]_2$. A suspension of *cis*-$[RuCl(bipy)_2\{N(O)SO_3\}]\cdot H_2O$ (0.03 g) in water (25 cm^3) was refluxed for 5 min, giving a clear red solution. This was cooled and NH_4PF_6 added until no further precipitate was formed. The solid *cis*-$[RuCl(bipy)_2(NO)][PF_6]_2$ product was collected by filtration, washed with water, ethanol, and diethyl ether, and dried in vacuum. Yield 0.02 g (50%). I.r. spectrum: ν(NO) at 1 930 cm^{-1} (lit.,[14] 1 931 cm^{-1}). Electronic spectrum (CH_3CN solution): 478 ($\varepsilon = 1.1 \times 10^2$), 320 ($1.3 \times 10^4$), and 290 nm ($1.6 \times 10^4$ dm^3 mol^{-1} cm^{-1}). A sample prepared by the literature method[14] showed absorption bands at 477 ($\varepsilon = 1.1 \times 10^2$), 323 ($1.4 \times 10^4$), and 295 nm ($2.0 \times 10^4$ dm^3 mol^{-1} cm^{-1}).

(*b*) *With aqueous hydrochloric acid: formation of cis*-$[RuCl(bipy)_2(NO)][PF_6]_2$. A suspension of $[RuCl(bipy)_2\{N(O)SO_3\}]\cdot H_2O$ (0.1 g) in aqueous hydrochloric acid (4 mol dm^{-3}, 20 cm^3) was set aside at room temperature overnight, over which period the solid dissolved giving an orange solution. Addition of NH_4PF_6 until there was no further precipitation gave orange crystals of *cis*-$[RuCl(bipy)_2(NO)][PF_6]_2$ (0.12 g, 90%) (Found: C, 30.8; H, 2.0; N, 8.7. Calc. for $C_{20}H_{16}ClF_{12}N_5OP_2Ru$: C, 31.2; H, 2.1; N, 9.1%). Electronic spectrum (CH_3CN): 478 ($\varepsilon = 1.3 \times 10^2$), 323 ($1.4 \times 10^4$), and 295 nm ($2.0 \times 10^4$ dm^3 mol^{-1} cm^{-1}). I.r. spectrum: ν(NO) at 1 930 cm^{-1}.

The same result was achieved when aqueous HNO_3 was used instead of HCl.

(*c*) *With aqueous ammonia: formation of* cis-*amminebis*(2,2′-*bipyridine*)*nitroruthenium hexafluorophosphate hydrate*, $[Ru(NH_3)(bipy)_2(NO_2)]PF_6\cdot H_2O$. A suspension of $[RuCl(bipy)_2\{N(O)SO_3\}]\cdot H_2O$ (0.15 g) in aqueous ammonia (4 mol dm^{-3}, 20 cm^3) was stirred at room temperature for 1 week, giving a red solution. This was filtered to remove unreacted starting material, excess of NH_4PF_6 was added, and the solution set aside. The red-black crystals of $[Ru(NH_3)(bipy)_2(NO_2)]PF_6\cdot H_2O$ which formed were collected by filtration, washed quickly with a mixture of ethanol and water, followed by diethyl ether, and dried in vacuum. The yield was low because of the high solubility of the product (Found: C, 38.0; H, 3.1; N, 13.2. Calc. for $C_{20}H_{21}F_6N_6O_3PRu$: C, 37.6; H, 3.6; N, 13.1%), I.r. spectrum: ν(NH) at 3 400—3 300 s, br cm^{-1}, $\delta(NH_3)$ at 1 625m,br cm^{-1}; identical to that observed from a sample prepared from aqueous NH_3 and $[RuCl(bipy)_2(NO)][PF_6]_2$. Electronic spectrum ($CH_3CN$ solution): 470 ($\varepsilon = 8.1 \times 10^3$), 336 ($9.6 \times 10^3$), and 289 nm ($6.1 \times 10^4$ dm^3 mol^{-1} cm^{-1}).

trans-*Chloro*(*nitrosylsulphito*)*tetra*(*pyridine*)*ruthenium*, *trans*-$[RuCl(py)_4\{N(O)SO_3\}]$.—To a solution of *trans*-$[RuCl(py)_4(NO)][ClO_4]_2$ (0.1 g) in water (7 cm^3) was added Na_2SO_3 (0.06 g). The colour of the solution immediately changed from orange to very dark green. On setting aside for 20 min at 5 °C a dark green powder precipitated. This was removed by filtration, washed with small amounts of water and ethanol and then with diethyl ether, and dried *in vacuo*. Yield 0.02 g (25%) (Found: C, 42.6; H, 3.55; N, 12.4. Calc. for $C_{20}H_{20}ClN_5O_4RuS$: C, 42.7; H, 3.6; N, 12.4%).

The dark green filtrate remaining after removal of $[RuCl(py)_4\{N(O)SO_3\}]$ was set aside at room temperature for 10 d. It changed colour to yellow within 24 h. Addition of NH_4PF_6 gave a yellow precipitate of *trans*-$[Ru(OH)(py)_4(NO)][PF_6]_2$. Yield 0.016 g (15%) (Found: C, 31.5; H, 2.7; N, 9.1. Calc. for $C_{20}H_{21}F_{12}N_5O_2P_2Ru$: C, 31.8; H, 2.8; N, 9.3%).

Reactions of trans-$[RuCl(py)_4\{N(O)SO_3\}]$.—(*a*) *With water: formation of* trans-*hydroxonitrosyltetra*(*pyridine*)*ruthenium bis*(*hexafluorophosphate*), *trans*-$[Ru(OH)(py)_4(NO)][PF_6]_2$. A suspension of *trans*-$[RuCl(py)_4\{N(O)SO_3\}]$ (0.03 g) in water (15 cm^3) was refluxed for 10 min on a steam-bath, giving a clear yellow solution. To this was added NH_4PF_6 until precipitation of the yellow crystalline product was complete. The *trans*-$[Ru(OH)(py)_4(NO)][PF_6]_2$ was removed by filtration, washed with small amounts of water and ethanol and then with diethyl ether, and dried *in vacuo*. Yield 0.025 g (63%). The i.r. spectrum of the product was identical to that of a sample prepared by the literature method [ν(NO)[12] at 1 868 cm^{-1}].

(*b*) *With aqueous hydrochloric acid; formation of* trans-*chloronitrosyltetra*(*pyridine*)*ruthenium bis*(*hexafluorophosphate*) *hemihydrate*, *trans*-$[RuCl(py)_4(NO)][PF_6]_2\cdot 0.5H_2O$. A suspension of *trans*-$[RuCl(py)_4\{N(O)SO_3\}]$ (0.1 g) in aqueous hydrochloric acid (4 mol dm^{-3}, 20 cm^3) was set aside at room temperature for 3 h. It was then filtered and excess of NH_4PF_6 added to the filtrate. On setting aside overnight yellow-orange crystals of $[RuCl(py)_4(NO)][PF_6]_2\cdot 0.5H_2O$ were formed, yield 0.08 g (60%) (Found: C, 30.7; H, 3.0; N, 8.7. Calc. for $C_{20}H_{21}ClF_{12}N_5O_{1.5}P_2Ru$: C, 30.7; H, 2.7; N, 8.95%). I.r. spectrum: ν(NO) at 1 903 cm^{-1} (lit.,[12] 1 910 cm^{-1}). Electronic spectrum: 438 ($\varepsilon = 1.6 \times 10^2$) and 256 nm ($1.4 \times 10^4$ dm^3 mol^{-1} cm^{-1}). A sample prepared by the literature method[12] showed absorption bands at 431 ($\varepsilon = 1.7 \times 10^2$) and 256 nm ($1.4 \times 10^4$ dm^3 mol^{-1} cm^{-1}).

Reaction between Penta-amminenitrosylruthenium Trichloride and Sulphite.—To a solution of $[Ru(NH_3)_5(NO)]Cl_3\cdot H_2O$ (0.07 g) and $NaHSO_3$ (0.97 g) in water (10 cm^3) were added four pellets (0.4 g) of NaOH. The final pH was *ca.* 12. After all the NaOH had dissolved excess of KI was added, producing a yellow precipitate. The spectral characteristics of the product indicated it contained a mixture of $[Ru(NH_3)_5(NO)]I_3\cdot H_2O$, $[Ru(NH_2)(NH_3)_4(NO)]I_2$, and $[Ru(NH_3)_5(NO_2)]I$ with traces of $[Ru(NH_3)_5(N_2)]I_2$ and $[Ru(OH)(NH_3)_4(NO)]I_2$. This mixture and the reactions causing it have been described previously.[10,11]

Instruments used in the preparative part of this work were Hitachi EPI-G2 and Perkin-Elmer 457 spectrophotometers for i.r. spectra (samples measured as KBr discs), and a Hitachi 624 for reflectance electronic spectra. Magnetic moments were obtained by the Gouy method and micro-

Table 6. Atomic positions (standard deviations in parentheses) for the non-hydrogen atoms of *cis*-[RuCl(bipy)$_2${N(O)SO$_3$}] *

Atom	x	y	z	Atom	x	y	z
Ru(1)	0.252 45(11)	0.419 86(6)	0.354 40(8)	C(23)	0.444 3(11)	0.542 9(10)	0.188 2(12)
Cl(1)	0.147 3(3)	0.428 2(3)	0.228 7(4)	C(24)	0.398 7(12)	0.605 8(9)	0.184 7(12)
N(1)	0.169 7(9)	0.359 7(8)	0.416 7(9)	C(25)	0.319 9(12)	0.613 6(8)	0.235 9(13)
O(1)	0.087 9(8)	0.370 4(7)	0.424 8(9)	C(26)	0.287 4(12)	0.559 4(9)	0.289 2(11)
S(1)	0.193 6(3)	0.274 7(2)	0.462 6(3)	N(31)	0.356 3(8)	0.412 7(6)	0.449 2(9)
O(2)	0.291 3(8)	0.274 7(6)	0.473 7(8)	C(32)	0.363 2(12)	0.446 7(9)	0.527 6(12)
O(3)	0.143 5(9)	0.271 4(7)	0.546 7(10)	C(33)	0.436 6(13)	0.439 3(10)	0.583 9(12)
O(4)	0.162 8(8)	0.231 3(6)	0.390 3(9)	C(34)	0.509 9(13)	0.397 2(9)	0.559 2(12)
N(11)	0.194 4(8)	0.510 4(6)	0.403 7(9)	C(35)	0.503 7(12)	0.363 5(9)	0.478 3(10)
C(12)	0.136 1(11)	0.513 0(9)	0.476 8(13)	C(36)	0.427 7(10)	0.370 7(8)	0.422 8(10)
C(13)	0.094 8(11)	0.574 3(10)	0.503 1(12)	N(41)	0.330 1(9)	0.343 2(6)	0.295 0(9)
C(14)	0.109 1(11)	0.633 3(9)	0.454 7(13)	C(42)	0.312 3(11)	0.308 4(9)	0.217 9(11)
C(15)	0.169 4(11)	0.626 8(8)	0.378 8(13)	C(43)	0.372 8(13)	0.264 6(10)	0.178 6(12)
C(16)	0.210 1(12)	0.567 0(8)	0.355 7(11)	C(44)	0.457 5(12)	0.256 5(9)	0.218 8(12)
N(21)	0.329 4(9)	0.497 4(7)	0.286 3(9)	C(45)	0.478 0(11)	0.291 4(9)	0.297 7(12)
C(22)	0.405 4(11)	0.489 4(9)	0.237 3(12)	C(46)	0.412 0(10)	0.332 2(8)	0.337 2(10)

* N(11),C(12)—C(16) comprise ring A of Figure 3, N(21),C(21)—C(26) ring A′, N(31),C(32)—C(36) ring B, and N(41),C(42)—C(46) ring B′. The numbering is sequential with the A–A′ ring junction between C(16) and C(26) and the B–B′ junction between C(36) and C(46).

analyses by the Institute of Chemical and Physical Research, Wako, Saitoma 351, Japan.

Vibrational Analysis.—The Wilson F and G matrix method [50] was used with a valency force field. The Ru{N(O)SO$_3$} structure was idealised from that found in *cis*-[RuCl(bipy)$_2${N(O)SO$_3$}] (Figure 3) by making RuNO(1)SO(2) strictly *trans*-planar and all the S–O distances, and O–S–O and N–S–O angles, internally equal. A calculation using the angles and distances actually observed rather than the idealised values showed that the calculated frequencies changed by less than 8 cm^{-1}. The force constants corresponding to the higher frequency vibrations were adjusted to give a best least-squares fit to the observed frequencies (17 observations, 8 adjusted constants). The fit was judged satisfactory when all (observed minus calculated) frequency differences were less than 10 cm^{-1}. For Fe{N(O)SO$_3$} the same structure was used except that the Fe–N distance was taken as 1.83 Å.

Determination of the Crystal Structure of cis-[RuCl(bipy)$_2${N(O)SO$_3$}] *by X-Ray Diffraction.*—Crystals of *cis*-[RuCl(bipy)$_2${N(O)SO$_3$}] were prepared as described above. However, a few small crystals which diffracted adequately were found in the yield of one preparation only after several preparations had produced crystals unsuitable for *X*-ray diffraction. One of these crystals, of dimensions 0.08 × 0.22 × 0.25 mm, was mounted in a thin-walled capillary tube and used for data collection. Neither the size nor the mosaicity of this crystal was optimal but no better material was found.

Weissenberg and precession photographs established the systematic absences $hk0$ for $h = 2n + 1$, $h0l$ for $l = 2n + 1$, and $0kl$ for $k = 2n + 1$ in the orthorhombic class, and the only possible space group was therefore *Pbca*.

The crystal was transferred to a Picker FACS 1 diffractometer and least-squares refinement of 12 accurately centred Friedel pairs of reflections with $2\theta > 30°$ was used to determine the cell dimensions.

Crystal data. $C_{20}H_{16}ClN_5O_4RuS$, $M = 559.0$, Orthorhombic, space group *Pbca*, $a = 14.479(19)$, $b = 19.493(17)$, $c = 14.490(13)$ Å, $U = 4\,090(13)$ Å^3, $Z = 8$, $D_c = 1.81$ Mg m^{-1}, $F(000) = 2\,240$, graphite monochromated, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 1.02 mm^{-1}. Because of the low μ no absorption correction was applied.

A unique data set was collected by the ω—2θ scan technique. Of 2 667 reflections with $2\theta < 45°$, 1 370 had $I > 2\sigma(I)$, and these were used for the structure determination. The low percentage of observed reflections was mainly due to the poor quality of the crystal.

After the usual corrections and reduction had been applied to the data the structure was obtained using the MULTAN approach [51] and refined using the NRC program package.[52] Scattering factors were taken from International Tables.[53] The final refinement, which minimised the function $\Sigma w(\Delta F)^2$ with $w = 1/[\sigma^2(|F|) + 0.005(|F|)^2]$, converged at R ($= \Sigma|\Delta F|/\Sigma|F_o|$) = 0.063 (0.142 including unobserved) and R' [$= (\Sigma|\Delta F|^2/\Sigma|F_o|^2)^{\frac{1}{2}}$] = 0.075 (0.092 including unobserved). All non-hydrogen atoms were included with fixed C–H distances (1.08 Å) and a fixed isotropic thermal parameter (total number of variables 290, an extinction parameter being included). A difference synthesis using the final parameters showed a highest positive peak of 0.96 e Å^{-3} (1.03 Å from Ru) and a lowest negative peak of -0.65 e Å^{-3}. Table 6 lists the non-hydrogen atom positions derived from the last cycle of refinement. Tables 3 and 4 give the bond distances and angles necessary for the discussion of the structure. The numbering scheme is shown in Figure 3.[54]

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