Preparation and Structure of Tetraphenylphosphonium Aquatetrachlorothionitrosylruthenate, $[PPh_4][Ru(NS)Cl_4(H_2O)]$ *

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The preparation and structural characterization of $[PPh_4][Ru(NS)Cl_4(H_2O)]$ are reported. Reaction of $S_3N_3Cl_3$ with ruthenium trichloride yielded a brown crude product $[Ru(NS)Cl_3]$. The salt $[PPh_4]$-$[Ru(NS)Cl_4(H_2O)]$ was prepared by the addition of PPh_4Cl to an aqueous solution of $[Ru(NS)Cl_3]$ followed by recrystallization of the brown precipitate from water–methanol (1 : 1). The crystals are triclinic, space group $P\bar{1}$, with unit-cell dimensions $a = 10.173(5)$, $b = 11.756(4)$, $c = 12.793(10)$ Å, $\alpha = 66.24(6)$, $\beta = 78.89(6)$, $\gamma = 72.58(4)°$, and $Z = 2$ (110 ± 2 K). The $[Ru(NS)Cl_4(H_2O)]^-$ anion forms an octahedron with H_2O *trans* to the thionitrosyl group. The Ru–N–S group is approximately linear [170.9(3)°] with Ru–N and N–S bond distances of 1.729(4) and 1.504(4) Å, respectively.

The preparation and study of thionitrosyl complexes is of current interest.[1] Four compounds have previously been studied by *X*-ray crystallography: $[Cr(\eta^5\text{-}C_5H_5)(CO)_2(NS)]$,[2] $[Mo(NS)(S_2CNMe_2)_3]$,[3] and $[M(NS)Cl_3(PPh_3)_2]$ (M = Ru or Os)].[4] Several anionic nitrosyl complexes have been synthesized and characterized,[5] but due to the present lack of a thionitrosylating agent, no synthesis of an anionic thionitrosyl complex has been described. We report here the first synthesis and structure of an anionic thionitrosyl complex $[PPh_4][Ru(NS)Cl_4(H_2O)]$.‡

Experimental

All chemicals used were of comparable purity. Tetrahydrofuran (thf) and n-hexane were dried by standard procedures, distilled, and deaerated just prior to use. The compound $S_3N_3Cl_3$ was prepared according to the literature method.[6]

Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer using KBr discs. Elemental analyses were performed by Beller Microanalytical Laboratory, Göttingen.

Preparation of Thionitrosylruthenium Trichloride, $[Ru(NS)Cl_3]$.—The compound $S_3N_3Cl_3$ (2.69 g, 11 mmol) in thf (30 cm^3) was added dropwise to a stirred solution of commercial ruthenium trichloride (2.25 g, *ca.* 10 mmol) in thf (100 cm^3) at room temperature under a nitrogen atmosphere. After the addition of $S_3N_3Cl_3$ was complete, the reaction mixture was stirred for 5 h. The resulting solution was filtered, and almost dried under reduced pressure. The brown residue was washed five times with n-hexane (20 cm^3) and dried in a vacuum desiccator over $CaCl_2$ for several days. This experiment was repeated four times and the formation of $[NH_4]_2$-$[Ru(NS)Cl_5]$ as a by-product in variable amounts with $[Ru(NS)Cl_3]$ [i.r. (Nujol): ν(NS) 1 290 cm^{-1}] was observed.

Preparation of Tetraphenylphosphonium Aquatetrachlorothionitrosylruthenate, $[PPh_4][Ru(NS)Cl_4(H_2O)]$.—Tetraphenylphosphonium chloride (3.0 g) in water (15 cm^3) was added to an aqueous solution of $[Ru(NS)Cl_3]$ (1.0 g in 50 cm^3). The brown precipitate which separated out was filtered off and dissolved in water–methanol (1 : 1, 50 cm^3). The brown precipitate is a mixture of $[PPh_4]_2[Ru(NS)Cl_5]$ and $[PPh_4]$-$[Ru(NS)Cl_4(H_2O)]$. The mixture was allowed to stand at room temperature for 10 d. The brown crystals, which were deposited on the wall, were filtered off and air dried {Found: C, 44.9; H, 3.30; N, 2.20; S, 4.70. Calc. for $[PPh_4][Ru(NS)Cl_4(H_2O)]$: C, 44.6; H, 3.40; N, 2.15; S, 4.95%}. I.r. (KBr): ν(NS) 1 318, ν(Ru–Cl) 305 cm^{-1}. For $[PPh_4]_2[Ru(NS)Cl_5]$, ν(NS) 1 300 cm^{-1}.

X-*Ray Data Collection and Structure Determination*.—A brown crystal with approximate dimensions 0.20 × 0.25 × 0.40 mm was sealed inside a glass capillary tube. All geometrical and intensity data were obtained from this crystal. The data collection was performed at low temperature to reduce the amount of librational motion. A temperature of 110 ± 2 K was maintained during the measurement by using an Enraf–Nonius universal low-temperature device. The cell constants were refined from the setting angles of 25 reflections with $10 \leqslant 2\theta \leqslant 24°$.

Crystal data.—$C_{24}H_{22}Cl_4NOPRuS$, triclinic, $M = 646.37$, space group $P\bar{1}$, $a = 10.173(5)$ Å, $b = 11.756(4)$, $c = 12.793(10)$ Å, $\alpha = 66.24(6)$, $\beta = 78.89(6)$, $\gamma = 72.58(4)°$, $U = 1\,332(1)$ Å^3, $Z = 2$, $D_c = 1.612$ g cm^{-3}, $F(000) = 648$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 11.35 cm^{-1}.

Reflections were measured in a hemisphere on an Enraf-Nonius CAD4 diffractometer and using a graphite monochromator. A broadening of the reflection profiles (ω scan mode, $2\theta_{max.} = 45°$) was observed on irradiation. Consequently a large scan width (3°) was chosen. Three standard reflections remeasured every 5 000 s decreased in intensity by about 20% during the measurement. The data were rescaled with respect to the standards. An empirical absorption

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* *Supplementary data available* (No. SUP 23949, 20 pp.): thermal parameters, H-atom co-ordinates, cation bond distances and angles, hydrogen bond parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

† Since the submission of this paper the following papers with anionic thionitrosyl complexes have been published: R. Weber, U. Müller, and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1983, **504**, 13; R. Weber and K. Dehnicke, *Z. Naturforsch., Teil B*, 1984, **39**, 262; K. K. Pandey, H. W. Roesky, M. Noltemeyer, and G. M. Sheldrick, *ibid.*, p. 590.

Table 1. Positional parameters and their estimated standard deviations

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	0.013 13(5)	0.224 14(4)	0.001 64(4)	C(10)	0.504 9(6)	1.220 0(5)	0.123 8(5)
Cl(1)	0.005 6(2)	0.048 4(1)	0.179 5(1)	C(11)	0.449 5(6)	1.149 8(5)	0.087 4(4)
Cl(2)	0.007 5(2)	0.385 4(1)	−0.184 1(1)	C(12)	0.446 8(6)	1.024 0(5)	0.158 0(4)
Cl(3)	−0.204 5(2)	0.339 3(1)	0.055 4(1)	C(13)	0.494 5(6)	0.714 7(5)	0.279 1(4)
Cl(4)	0.217 1(2)	0.099 0(1)	−0.063 0(1)	C(14)	0.618 1(6)	0.637 7(5)	0.250 9(4)
S	0.141 4(2)	0.377 6(1)	0.099 6(1)	C(15)	0.615 4(6)	0.563 2(5)	0.190 2(4)
P	0.496 1(2)	0.810 7(1)	0.358 4(1)	C(16)	0.491 2(7)	0.565 2(5)	0.161 0(4)
O	−0.101 5(4)	0.144 6(3)	−0.060 0(3)	C(17)	0.367 9(6)	0.645 0(5)	0.185 3(5)
N	0.093 8(5)	0.299 1(4)	0.053 0(4)	C(18)	0.369 0(6)	0.719 4(5)	0.245 5(5)
C(1)	0.344 7(6)	0.809 7(5)	0.457 5(4)	C(19)	0.647 9(6)	0.743 3(5)	0.436 3(4)
C(2)	0.271 5(6)	0.922 2(5)	0.476 5(4)	C(20)	0.773 8(7)	0.766 7(5)	0.378 7(5)
C(3)	0.161 7(7)	0.917 8(5)	0.560 8(5)	C(21)	0.892 0(6)	0.710 1(6)	0.435 9(5)
C(4)	0.121 8(7)	0.804 2(5)	0.623 1(5)	C(22)	0.883 8(7)	0.633 1(6)	0.551 1(5)
C(5)	0.192 6(6)	0.693 3(5)	0.602 9(5)	C(23)	0.759 8(7)	0.612 1(6)	0.609 2(6)
C(6)	0.304 8(7)	0.696 0(5)	0.519 6(5)	C(24)	0.641 1(6)	0.666 6(6)	0.552 2(5)
C(7)	0.498 4(6)	0.971 6(5)	0.264 8(4)	H(25)	−0.0488	0.1074	−0.1171
C(8)	0.552 5(6)	1.044 3(5)	0.301 7(4)	H(26)	−0.1250	0.0839	0.0000
C(9)	0.555 4(7)	1.168 3(5)	0.230 2(5)				

Table 2. Bond angles (°) in the anion

Cl(1)–Ru–Cl(2)	172.76(5)	Cl(2)–Ru–N	93.00(12)
Cl(1)–Ru–Cl(3)	90.38(5)	Cl(3)–Ru–Cl(4)	173.06(5)
Cl(1)–Ru–Cl(4)	89.88(4)	Cl(3)–Ru–O	85.25(9)
Cl(1)–Ru–O	86.95(8)	Cl(3)–Ru–N	89.88(13)
Cl(1)–Ru–N	94.24(12)	Cl(4)–Ru–O	87.84(9)
Cl(2)–Ru–Cl(3)	89.84(4)	Cl(4)–Ru–N	97.02(13)
Cl(2)–Ru–Cl(4)	89.03(4)	O–Ru–N	175.00(15)
Cl(2)–Ru–O	85.86(8)	Ru–N–S	170.9(3)

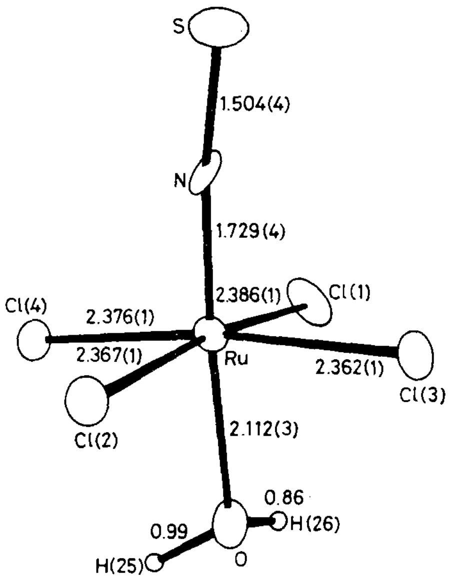

Figure 1. Perspective view of the anion giving the bond distances (Å)

correction was made, based on the psi-scans of two reflections. Of the total number of reflections (3 483), 3 243 were independent and 2 644 with $F^2 > 2\sigma(F^2)$ were regarded as 'observed.'

The structure was determined by Patterson and Fourier methods and refined by full-matrix least squares. It was found to be centrosymmetric, thus the space group is $P\bar{1}$. Positions for the H atoms of the phenyl groups were calculated while those of the water molecule were taken from a difference synthesis. The H atoms were not refined. Extinction was found to be negligible. Scattering factors and corrections for anomalous dispersion were taken from ref. 7. Use of a weighting scheme of the form $w(F) = 1/[\sigma^2(F) + (0.015F)^2]$ led to final $R(= \Sigma||F_o| - |F_c||/\Sigma|F_o|)$ and $R' \{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}\}$ values of 0.040 and 0.041. The calculations were performed with the SDP program system. A final difference synthesis showed a density of up to 0.6 e Å^{-3} near the Ru atom but was otherwise featureless. The resulting positional parameters are given in Table 1.

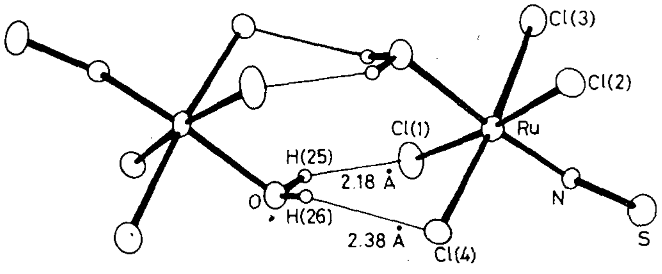

Figure 2. Perspective view of the dimer formed from two anions by hydrogen bonding

Results and Discussion

The compound $S_3N_3Cl_3$ reacts with ruthenium trichloride in thf to give thionitrosylruthenium trichloride [Ru(NS)Cl_3] together with variable amounts of $[NH_4]_2$[Ru(NS)Cl_5]. Addition of PPh_4Cl to an aqueous solution of [Ru(NS)Cl_3] initiated precipitation of the brown product $[PPh_4]_2$[Ru(NS)Cl_5] (90%) and [PPh_4][Ru(NS)Cl_4(H_2O)]. Recrystallization of the brown product from water–methanol produces brown crystals of [PPh_4][Ru(NS)Cl_4(H_2O)]. Infrared studies of the latter revealed a strong NS band at 1 318 cm^{-1} compared to 1 300 cm^{-1} for $[PPh_4]_2$[Ru(NS)Cl_5]. This shift to higher frequency with decreasing formal negative charge on the complex is comparable with the behaviour observed for related metal nitrosyl compounds.[5] In the case of hydrolysis of $[Ru(NO)Cl_5]^{2-}$, for which the kinetic data are available,[8–10] the stereochemistry of the initial substitution product is unknown, but it is noteworthy that this substitution requires a temperature of 50 °C. For $[Ru(NS)Cl_5]^{2-}$, substitution occurs immediately at room temperature and in *trans* position with respect to the NS group.

The Structure of [PPh_4][$Ru(NS)Cl_4(H_2O)$].—The structure consists of [$Ru(NS)Cl_4(H_2O)$]$^-$ anions and tetraphenylphosphonium cations. The geometry of the anion together with bond distances is shown in Figure 1; the bond angles are given in Table 2. The Ru atom is octahedrally co-ordinated by four equatorial Cl atoms, a NS group bonding *via* nitrogen, and an H_2O molecule. Two [$Ru(NS)Cl_4(H_2O)$]$^-$ groups form centrosymmetric dimers *via* O–H ··· Cl hydrogen bonds (Figure 2). The dimers are interconnected by Cl ··· S van der Waals contacts [S ··· Cl(2) 3.240(2) and S ··· Cl(3) 3.300(2) Å]. Between the atoms of the anion and the tetraphenylphosphonium group there is no interaction shorter than the sum of the van der Waals radii.

The average equatorial Ru–Cl bond length of 2.373(1) Å is in good agreement with the corresponding value of 2.376(2) Å in the [$Ru(NO)Cl_5$]$^{2-}$ anion.[11] The N–S bond distance of 1.504(4) Å is similar to that in the thionitrosylosmium complex [$Os(NS)Cl_3(PPh_3)_2$], 1.504(11) Å, but longer than that in $NS^+Sb_2F_{11}^-$, 1.42(1) Å.[12] The longer N–S distance in [$Ru(NS)Cl_4(H_2O)$]$^-$ in comparison to the NS^+ cation might be explained by considerable π-back bonding from Ru to NS.

The axial Ru–O bond distance of 2.112(3) Å is much longer than the calculated value of the covalent radii[13] of Ru^{II} and O, 1.99 Å. As a consequence the average O–Ru–Cl angle of 86.5° is smaller than the average N–Ru–Cl angle of 93.5°. The Ru–N–S angle of 170.9(3)° demonstrates that the NS group is bonded nearly linearly to the metal.

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