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Disulphidothionitrate Nitrosyl Complexes of Ruthenium(II)

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Abstract

The complexes $Ru(NO)X_3L_2$ (X = Cl or Br; L = PPh_3 or $AsPh_3$) react with heptasulfurimide (S_7NH) in dimethylformamide to afford disulphidothionitrate (S_3N^-) complexes $Ru(NO)(S_3N)X_2L$. The reactions of $Ru(NO)X_3 \cdot 2H_2O$ (X = Cl, I) with S_7NH in methanol produce six coordinated $\{RuNO\}^6$ complexes $Ru(NO)(S_3N)_2X$. The complexes are characterised by elemental analyses, magnetic measurements, infrared and electronic spectral studies.

Introduction

Considerable attention has been given to the chemistry of synthetic transition metal complexes complexed by unstable small inorganic sulfur–nitrogen ligands such as thionitrosyl, thiazate and thionitro [1, 2]. A few transition metal complexes of the disulphidothionitrate (S_3N^-) ligand have previously been prepared from S_4N_4 [3–9] or $[(Ph_3P)_2N^+][S_3N^-]$ [10–12]. We have recently reported a new synthetic route, for disulphidothionitrato complexes by reaction of S_7NH with metal complexes [13], which has been utilized for the synthesis of S_3N^- complexes [14–16]. Chivers and coworkers called the S_3N^- ion a thio analogue of peroxynitrite [12]; we named it disulphidothionitrate [13]. Herein we wish to report the synthesis of the first complexes of ruthenium(II) with the S_3N^- ligand by the reaction of ruthenium nitrosyl complexes with S_7NH.

Experimental

All the reagents used were of analytical or chemical pure grade. The solvents were dried by standard methods. Every reaction was carried out under pure dry nitrogen atmosphere. The ruthenium nitrosyl complexes $Ru(NO)X_3L_2$ and $Ru(NO)X_3 \cdot 2H_2O$ were prepared by literature methods [17, 18]. S_7NH was prepared from sulfurmonochloride and ammonia in DMF by the literature method [19]. The purified S_7NH had a melting point of 113 °C and was used for the reactions. Melting points were taken in capillaries and are uncorrected.

Carbon, hydrogen and nitrogen in the complexes were analysed by the microanalytical laboratory of this department. The analysis for chloride, bromide, iodide and sulfur was carried out by standard methods [20]. For the phosphorus and arsenic estimation, the samples were decomposed with sodium peroxide, sugar and sodium nitrate in the ratio 20:1:3 and estimations were performed by standard methods [21]. The results of these analyses appear in Table I. The IR spectra were recorded

TABLE I. Elemental Analyses of the Complexes (numbers in parenthesis are calculated values)

Compound	C	H	N	X	S	P/As
$Ru(NO)(S_3N)Cl_2(PPh_3)$	37.5	2.8	4.9	12.2	16.9	5.6
	(37.63)	(2.61)	(4.87)	(12.36)	(16.72)	(5.4)
$Ru(NO)(S_3N)Br_2(PPh_3)$	32.7	2.4	4.4	24.3	14.6	4.8
	(32.57)	(2.26)	(4.22)	(24.13)	(14.47)	(4.67)
$Ru(NO)(S_3N)Cl_2(AsPh_3)$	35.0	2.5	4.6	11.5	15.4	12.2
	(34.95)	(2.42)	(4.53)	(11.48)	(15.53)	(12.13)
$Ru(NO)(S_3N)Br_2(AsPh_3)$	30.4	2.3	4.1	22.8	13.6	10.6
	(30.55)	(2.12)	(3.96)	(22.63)	(13.57)	(10.60)
$Ru(NO)(S_3N)_2Cl$			10.8	9.4	49.8	
			(10.86)	(9.18)	(49.67)	
$Ru(NO)(S_3N)_2I$			8.9	26.8	40.4	
			(8.78)	(26.56)	(40.16)	

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with a Perkin-Elmer model 580 spectrophotometer in the range 4000–250 cm^{-1}. The electronic spectra of the samples were recorded in dichloromethane solution on a Varian 634S spectrophotometer. Magnetic measurements were made with a Gouy balance at room temperature. All the complexes were found to be diamagnetic.

Reactions of S_7NH with $Ru(NO)X_3L_2$ ($X = Cl$ or Br; $L = PPh_3$ or $AsPh_3$)

The experiments were performed similarly and the reaction of $Ru(NO)Cl_3(PPh_3)_2$ with S_7NH is described as a representative example.

To a stirred orange solution of $Ru(NO)Cl_3(PPh_3)_2$ (0.2 g) in DMF (10 ml) was added a blue solution of S_7NH (0.065 g) in DMF (10 ml). The reaction mixture was stirred for 6 h. The solvent was evaporated to 5 ml under reduced pressure. On addition of methanol–water (3:1) (100 ml), a brown complex separated out which was centrifuged, washed with methanol and diethylether and dried under vacuum. It was dissolved in dichloromethane (10 ml) and filtered. On addition of n-hexane (50 ml), a brown complex $Ru(NO)(S_3N)Cl_2(PPh_3)$ separated out, was centrifuged, washed with n-hexane and dried under vacuum (yield 58 mg, 38%). Triphenylphosphine sulphide was isolated from the washings.

The other similar coloured complexes were isolated in yield of 40%, $[Ru(NO)(S_3N)Br_2(PPh_3)]$; 35% $[Ru(NO)(S_3N)Cl_2(AsPh_3)]$; 32%, $[Ru(NO)(S_3N)Br_2(AsPh_3)]$.

Reactions of S_7NH with $Ru(NO)X_3{\cdot}2H_2O$ ($X = Cl, I$)

To a stirred solution of $Ru(NO)X_32H_2O$ (0.2 g) in methanol (30 ml) was added a blue solution of S_7NH (0.160 g) in DMF (15 ml). The reaction mixture was stirred for 5 h. The solvent was evaporated to 5 ml under reduced pressure. On addition of methanol–water (3:1) (100 ml), a brown product precipitated which was centrifuged, washed with cold methanol and ether and dried under vacuum. During the recrystallization from dichloromethane and n-hexane, the brown product changed to a black solid, which analysed for $Ru(NO)(S_3N)_2X$ ($X = Cl$ or I). In five successive experiments the yield of the black compounds has been found to be 10–15%.

Results and Discussion

S_7NH reacts with $Ru(NO)X_3L_2$ ($X = Cl$ or Br; $L = PPh_3$ or $AsPh_3$) to give disulphidothionitrato complexes $[Ru(NO)(S_3N)X_2L]$. The heptasulfurimide dissolves in DMF to give a blue solution and the blue species has been characterized as the NS_4^- anion [22] (eqn. (1))

$$S_7NH \underset{}{\overset{DMF}{\rightleftharpoons}} S_4N^- + 0.75S_8 + H^+ \qquad (1)$$

The S_4N^- anion reacts with triphenylphosphine to give the S_3N^- anion and $SPPh_3$ [12] (eqn. (2))

$$S_4N^- + PPh_3 \longrightarrow S_3N^- + SPPh_3 \qquad (2)$$

The reactions of $Ru(NO)X_3L_2$ with S_7NH may therefore be represented by (eqn. (3))

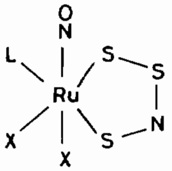
$$Ru(NO)X_3L_2 + S_7NH \xrightarrow{DMF}$$

$$Ru(NO)(S_3N)X_2L + 3/8S_8 + SL + H^+ + Cl^- \qquad (3)$$

Similarly the reactions of S_7NH with $Ru(NO)X_3{\cdot}2H_2O$ ($X = Cl$ or I) give disulphidothionitrato complexes $Ru(NO)(S_3N)_2X$ in low yield (eqn. (4)).

$$Ru(NO)X_3 + 2S_7NH \longrightarrow Ru(NO)(S_3N)_2X + \ldots \qquad (4)$$

The complexes $Ru(NO)(S_3N)X_2L$ ($X = Cl$ or Br; $L = PPh_3$ or $AsPh_3$) are air stable, brown diamagnetic solids. The IR spectra (Table II) of these complexes contain a strong band in the range 1835–1845 cm^{-1} due to ν(NO) stretching absorption which occurs at *ca.* 35 cm^{-1} lower than that for precursor nitrosyl complexes $Ru(NO)X_3L_2$. The bands in the regions 1000–1020 and 700–745 cm^{-1} due to ν(NS) and 592–600 cm^{-1} due to ν(S–S) are in close agreement with the values for the coordinated bidentate S_3N^- ligand reported in the literature [8, 9, 12, 13]. The low frequency IR spectra of these complexes have two bands in the range 345–290 cm^{-1} which are assigned to ν(Ru–Cl). The absorption at the highest energy is assigned to the ν(Ru–Cl) stretch *trans* to the nitrosyl group and at a lower energy is assigned to the ν(Ru–Cl) stretch *trans* to the S_3N^- ion. The corrected nitrosyl stretching frequency according to Ibers' rules [23] falls above 1620 cm^{-1}, which indicates a linear bonding of the nitrosyl group. The diamagnetic behaviour and linear bonding mode of the nitrosyl group suggest that the oxidation state of the metal ion is +2 and these complexes are regarded as complexes between Ru(II) and NO$^+$. It is, therefore, possible to assign the following structure to $\{RuNO\}^6$:



Ruthenium ion, thus, has an electronic configuration t_{2g}^6 transforming as $^1A_{1g}$. Excitation of an electron to the e_g orbital yields the configuration $t_{2g}^5\ e_g^1$ which spans $^3T_{1g} + {}^1T_{1g} + {}^1T_{2g} + {}^3T_{2g}$ with the spin-triplet state lying at a lower energy than the singlet. Their electronic spectra should show four

TABLE II. Colour, Melting Point and Important Infrared Frequencies of the Complexes

Compounds	Colour	Melting point (°C)	ν(NO) (cm^{-1})	Bands due to S_3N^- ligand (cm^{-1})
$Ru(NO)(S_3N)Cl_2(PPh_3)$	brown	220	1840	1020 745 592
$Ru(NO)(S_3N)Br_2(PPh_3)$	brown	235	1835	1020 742 600
$Ru(NO)(S_3N)Cl_2(AsPh_3)$	brown	222	1838	1003 739 600
$Ru(NO)(S_3N)Br_2(AsPh_3)$	brown	236	1834	1001 735 600
$Ru(NO)(S_3N)_2Cl$	black	>360	1845	1025 745 700 473
$Ru(NO)(S_3N)_2I$	black	>360	1840	1020 740 700 473

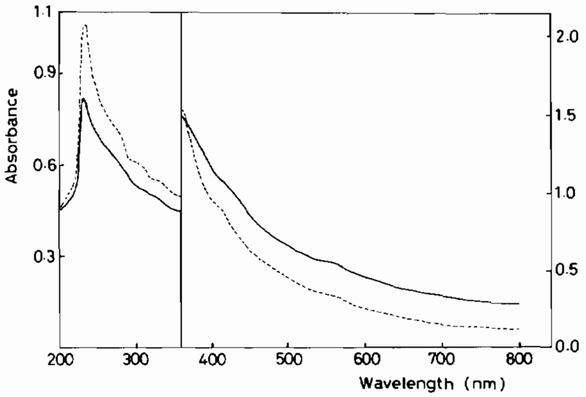
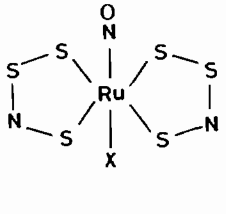


Fig. 1. Absorption spectra of $Ru(NO)(S_3N)Cl_2(PPh_3)$ (———) and $Ru(NO)(S_3N)Br_2(PPh_3)$ (------) (*ca.* 10^{-4} M solution for visible; 10^{-5} M solution for UV in dichloromethane).

d–d transition bands (two spin allowed and two spin forbidden). The visible spectra of the complexes showed two bands around 18000 cm^{-1} and 24000 cm^{-1} (Fig. 1). However, the extinction coefficients of these bands are higher (~10^3) as compared to the ones found normally for the octahedral complexes. These bands may be d–d singlet to singlet transitions in which case the intensity of the bands may arise due to (i) the covalent nature of the complex and (ii) the lowering of the symmetry of the molecule whereby the center of symmetry is lost. On the other hand, these bands may arise due to charge transfer or π–π^* transitions of the S_3N^- ligand [8]. The complexes $Ru(NO)(S_3N)_2X$ (X = Cl or I) are air stable, diamagnetic solid and insoluble in most of the organic solvents. The IR spectrum of $Ru(NO)(S_3N)_2Cl$ shows absorption bands at 1845 cm^{-1} due to ν(NO), at 1025, 745, 700 cm^{-1} due to ν(NS), at 473 cm^{-1} due to ν(Ru–S) and at 340 cm^{-1} due to ν(Ru–Cl). The IR spectrum of $Ru(NO)(S_3N)_2I$ shows absorption bands at 1840 cm^{-1} due to ν(NO) at 1020, 740, 700 cm^{-1} due to ν(NS) and at 473 cm^{-1} due to ν(Ru–S). The IR absorption bands due to the S_3N^- ligand are in close agreement with values for the bidentate S_3N^- ligand. The diamagnetic behaviour, linear bonding mode of the nitrosyl group and bidentate bonding mode of the S_3N^- ligand suggest the following structure for these complexes:



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