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Hexakisamine-and Benzonitrilepentakisamine-Complexes of Ruthenium(II) . The Ruthenium Induced Activation of Amines to Oxidation

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The synthesis is reported of a range of complexes of the type $Ru^{II}L_6X_2 . nH_2O$ and $Ru^{II}L_5(NCPh)X_2$ where L represents a primary amine of the type $R . CH_2 . NH_2$ and X a univalent anion. The infra-red spectra are discussed and it is noted that the spectral frequencies are sensitive both to amine and the anion X, however for the higher amines ν(CN) for benzonitrile is on average 20 cm^{-1} lower than in the corresponding ammine complexes. The hexakisamine-complexes react with dioxygen to give products containing materials (cyanide or nitrile) derived from the oxidation of the co-ordinated amine. The stoicheiometry of the reaction is established in the methylamine case.

Introduction

It would be desirable industrially to establish new routes for the reduction of nitriles to primary amines. Since there appear to be similarities between the inraction of metal ions with nitriles, and the same ions with dinitrogen,[1-4] we decided to study complexes of nitriles with metal centres capable of co-ordinating dinitrogen, in the hope of finding new types of reactivity. The recent finding[5] that a water soluble cobalt-porphyrin, a nitrogenase model, will catalyse the reduction of acetonitrile by borohydride in an aqueous medium supports the concept behind our approach. In this paper we consider the synthesis and spectra of the complexes $Ru^{II}L_5(NCPh)^{2+}$, where we find it convenient to select benzonitrile as a specific nitrite and L which is a primary aliphatic amine. We also consider some previously unknown hexakisamine complexes of ruthenium(II).

Early in our work, we observed that hexakisamine complexes of ruthenium(II) react readily with molecular oxygen to afford cyano-complexes (CH_3NH_2) or nitriles (RCH_2NH_2). A preliminary report of this observation has already appeared.[6] Similar ligand reactivity has been reported[7,8] for ethylenediamine co-ordinated to Ru^{II} and Fe^{II}. In this paper we report our observations in more detail.

Experimental Section

Reagents. Comercial samples of benzonitrile and aliphatic amines were used. Methylamine was supplied as a 25% aqueous solution. The purity of the higher amines was checked by GLC before use.

Synthesis. Analytical data and other criteria of purity are gathered into Table I.

Hexakis(amine)ruthenium(II) salts. The only satisfactory method of preparation to be found was based on that developed by Powell and Lever[9] for ruthenium(II) ammine complexes. All syntheses must be carried out under argon. A typical procedure was as follows: ruthenium trichloride[a] (0.1 g) in distilled water (25 ml) was mixed with n-butylamine (10 ml) under argon. The mixture was treated with zinc dust (0.1 g) and refluxed under argon until the solution assumed a pale green colour (approx. lh.). The warm solution was filtered into a clean flask and treated with a saturated acqueous solution containing a simple salt of an appropriate counter ion (e.g. KBr, KI, or $NaBF_4$). *Caution*: perchlorate affords explosively unstable compounds.

The following modifications to the above procedure should be noted:

(a) When chloride salts were required, hydrochloric acid was added prior to the addition of excess amine and zinc dust.

(b) In the case of ethylamine, if an excess of bromide ions are present, the desired complex is precipitated during the reaction and is filtered with the excess zinc dust.

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[a] Commercial specimen.
[7] B.C. Lane, J.E. Lester, and F. Basolo, *Chem. Comm.*, 1618 (1971).
[8] V.L. Goedken, *J.C.S. Chem. Comm.*, 207 (1972).
[9] F.M. Lever and A.R. Powell, *Chem. Soc. Special Publications*, No 12 (Lon. 1959) p. 135.

Table I. Analytical Data for Hexakis (amine) complexes of Ruthenium(II).

Complex	Calculated % C	% H	% N	% X	Found % C	% H	% N	% X	Λ_M ($10^{-3}M$ solns.)[a]
$[Ru(MeNH_2)_6]Br_2$	16.1	6.7	18.8	35.6	16.4	6.6	18.8	33.8	204
$[Ru(MeNH_2)_6]I_2$	13.3	5.5	15.5	47.13	12.9	5.2	15.4	—	
$[Ru(MeNH_2)_6](BF_4)_2$	15.6	6.5	18.2	—	15.8	6.1	18.5	—	
$[Ru(EtNH_2)_6]I_2$	23.0	6.7	13.4	40.4	22.4	6.5	12.6	38.0	
$[Ru(Pr^nNH_2)_6]I_2$	30.4	7.6	11.8	34.4	31.1	7.8	12.2	35.1	
$[Ru(Bu^nNH_2)_6]Cl_2$	47.2	10.8	13.8	11.7	45.8	10.5	13.5	11.5	194
$[Ru(Bu^nNH_2)_6]Br_2$	41.1	8.8	12.0	23.0	40.2	8.6	12.0	23.4	
$[Ru(Bu^nNH_2)_6]I_2$	36.4	8.3	10.6	31.9	35.5	7.9	10.6	31.1	
$[Ru(Bu^nNH_2)_6](BF_4)_2$	40.4	9.2	11.8	—	39.3	8.9	11.6	—	
$[Ru(Bu^iNH_2)_5(H_2O)]Cl_2$[b]	44.1	10.4	12.9	13.1	42.0	9.5	13.0	12.7	198
$[Ru(Bu^iNH_2)_6]Br_2 . 5H_2O$	36.5	9.6	10.7	20.2	36.1	8.1	10.8	18.4	
$[Ru(Bu^iNH_2)_6]I_2 . 8H_2O$	30.8	8.8	9.0	27.1	30.1	7.0	9.1	26.9	
$[Ru(Am^iNH_2)_6]Cl_2 . 2H_2O$	49.0	10.8	11.7	9.0	49.7	11.3	11.6	9.8	210
$Ru(CN)_3 . H_2O$	18.2	1.0	21.3	—	18.1	1.9	21.2	—	Insoluble

[a] $10^{-3}M$ $[Ni(en)_3](NCS)_2$ gives Λ_M = 226. [b] This complex is extremely reactive in the presence of light or oxygen and it was difficult to obtain reliable analytical data. ν(OH) 3385 and 3540 cm^{-1}.

(c) Use of branched chain primary amines e.g. *iso*-butylamine or *iso*-amylamine gives unstable products one of which, $Ru(^iBuNH_2)_5(H_2O)Cl_2$, appears to be a pentakis(ammine)-complex (see Table I).

(d) The presence of acid was required during the reduction stage for the methylamine and ethylamine preparations.

Benzonitrilepentakis(methylamine)ruthenium(II) di-iodide. $[Ru(MeNH_2)_6]Br_2$ (0.01 g) was dissolved in a mixture of water (5 ml), 2N sulphuric acid (1 ml) and ethanol (6 ml). One drop of benzonitrile was added and the mixture was heated, under argon, on a water bath. The colour changed to dark yellow at which stage zinc dust was added to the reaction vessel which was then set aside for 10 min. The mixture was filtered and the volume of the filtrate reduced to 4 ml in a rotatory film evaporator. Addition of a saturated solution of KI afforded a yellow complex which was washed carefully with water. ethanol and ether.

Benzonitrilepentakis-n-propylamineruthenium(II) dibromide. A mixture containing ruthenium trichloride (0.1 g) in distilled water (20 ml), n-propylamine (12 ml) and zinc dust (0.1 g) was stirred at 40° under an atmosphere of argon until the colour of the solution was pale green. Benzonitrile (0.05 ml) in n-propylamine (3 ml) was injected through a serum cap into the reaction flask. The solution immediately became orange-yellow in colour and was filtered into a cooled flask. Addition of dilute hydrobromic acid to the filtrate afforded the complex. The product was washed with water and dried in vacuo over P_4O_{10}.

Benzonitrilepentakis-n-butylamineruthenium(II) salts. $[Ru(NH_2Bu^n)_5(NCPh)]X_2$, $X^- = Cl^-, Br^-, I^-, BF_4^-$. A mixture of ruthenium trichloride (0.1g) in distilled water (25 ml), n-butylamine (12 ml) and zinc dust (0.1 g) was refluxed under argon until the solution was pale green and some zinc adhered firmly to the side of the flask. Benzonitrile (0.05 ml) in n-butylamine (2 ml) was injected through a serum cap into the reaction flask. When the solution colour became orange-yellow the contents of the flask were rapidly filtered Dilute hydrochloric acid was added to the filtrate until a slight turbidity was produced, this was removed by addition of a little n-butylamine. The solution was divided into four parts and each treated with a saturated solution of an appropriate salt (KCl, KBr, KI, or $NaBF_4$). The *products* were washed with distilled water and dried in vacuo over P_4O_{10}.

Benzonitrilepentakis-iso-butylamineruthenium(II) salts, $[Ru(NH_2Bu^i)_5(NCPh)]X_2$, $X^- = Cl^-, Br^-, I^-$. The above method, using similar quantities of materials, was followed with the modification that the original reaction mixture was held at 60°. The products were precipitated with dilute acids care being, to ensure that the solutions remained alkaline. The complexes were washed with distilled water and dried in vacuo over P_4O_{10}.

Benzonitrilepentakis-iso-amylamineruthenium(II) dibromide. The method was identical with that for the corresponding n-butyl-amine salts. The product was finally precipitated with a mixture of dilute hydrobromic acid and potassium bromide and was dried in vacuo over P_4O_{10}.

Dinitrogenpentakisamineruthenium(II) complexes. If argon is replaced by dinitrogen in the preparation of hexakispropylamine-ruthenium(II), and in preparations involving higher amines, the products are contaminated with small quantities of the dinitrogenpentakisamineruthenium(II) complexes. The infra-red stretching frequency for co-ordinated dinitrogen was noted but no attempt was made to isolate the complexes in yield sufficient for detailed physical investigation. It is of interest that in the case of the methylamine and ethylamine preparations even deliberate attempts to achieve the synthesis of dinitrogen complexes from dinitrogen gas failed; an indirect route via azide ion was also unsuccessful.

The reaction of hexakismethylamineruthenium(II) salts with dioxygen. As noted previously when samples of the hexakismethylamineruthenium(II) complexes are left exposed to air they become black and the infra-red spectrum changes, in particular a new band centred at 2040 cm^{-1} appears. In addition evidence for the formation of water and methylammonium ions is found. Quantitative extraction of the black material with nitromethane and subsequent crystallisation affords the methylammonium salt, $MeNH_3^+X^-$ corresponding to the counter anion present in the initial ruthenium complex. The identity of the methylammonium salts was established by elemental analysis and by infra-red and mass spectroscopy.

That oxygen was necessary for the degradation to occur was established by sealing a specimen of $Bu(MeNH_2)_6I_2$ under dry, oxygen free, nitrogen in a gas uptake apparatus.[10] No nitrogen was consumed and no change in the i.r. spectrum of the solid occurred. Similarly when a known weight of solid was dissolved in water under nitrogen, no gas was taken up; however on the introduction of oxygen to the apparatus 3.25 mole of dioxygen per mole of ruthenium complex was reproducibly consumed.

The nature of the oxidation product. Removal of the methylammonium salts from the black solids obtained from oxidative degradation of the solid complexes $Ru(MeNH_2)_6X_2$ (X = Br, I) afforded an insoluble and intractable material which gave an infrared spectrum consistent with the presence of only water and a species absorbing at 2040 cm^{-1}. A typical analysis suggested the formula $Ru(CN)_3 . 3H_2O$ (Found: C, 15.8; H, 1.6; N, 17.5. $C_3H_6N_3O_3Ru$ requires C, 15.5; H, 2.2; N, 18.1%). A cleaner method of preparation is to allow an aqueous solution of the hexakis(methylamine)ruthenium(II) salt to consume oxygen (vide supra) when the complex precipitates from solution during the course of the reaction. It is found that two molecules of water are readily lost at 110°C to give $Ru(CN)_3 . H_2O$ (Table I). The possibility that the band at 2040 cm^{-1} in the i.r. spectrum of the oxidation product was due to a ruthenium hydride species was considered. However ,when the oxidised material was treated with concentrated acid no hydrogen gas was evolved.

Deuteration of $Ru^{II}(NH_2CH_3)_6I_2$. Potassium chlororuthenite (0.05 g) in concentrated hydrochloric acid (1 ml) was diluted with deuterium oxide (3 ml) and treated with a 25% solution of methylamine in water (3 ml). The mixture was reduced under argon with zinc dust, filtered and treated with an excess of potassium iodide (in D_2O) to afford a yellow *precipitate.* The infra-red spectrum confirmed that deuteriation of the amino-groups had occurred, however some coordinated CH_3NH_2 was still present. Found C, 12.8; N, 14.9 $C_6H_{18}D_{12}I_2N_6Ru$ requires C, 13.0; N, 15.2%. On oxidative degradation the band at 2040 cm^{-1} appeared but no counterpart at 1407 cm^{-1} was seen. Thus it is improbable that the material contains ruthenium to hydrogen bonds and if it does the hydrogen must be derived from the methyl group.

Degradation of complexes of the higher amines. Reaction of the hexakisamineruthenium(II) complexes of the higher amines, RCH_2NH_2, with oxygen or air afforded dark tar like materials which gave strong i.r. bands above 2000 cm^{-1} consistent with the presence of nitrile. These materials are complex mixtures which have defied separation and analysis. That nitriles are indeed formed is suggested by the fact that, if in a typical preparation of $Ru(Bu^nNH_2)_6Cl_2$ (vide supra) half the reaction mixture is treated with HCl under argon to give $Ru(Bu^nNH_2)_6Cl_2$ and the other half is treated with propyl cyanide and HCl to afford $Ru(Bu^nNH_2)_5(NCPr^n)Cl$, nitrile bands appear in the spectrum of the hexakis complex after exposure to oxygen at the same frequency (2205 cm^{-1}) as that of coordinated n-propylcyanide in the pentakis complex.

The complexes of iso-butylamine were the least stable of those considered in this paper. The chloride in particular, which analysis suggested to be aquopentakis(isobutylamine)ruthenium(II) chloride, degraded very rapidly indeed. However the material was relatively stable when sealed under argon in the absence of light. In the presence of sunlight or U.V. oxidation is fast even in a limited supply of oxygen and it appears that, in this case photo-oxidation is important but the presence of oxygen is essential for nitrile formation. In the case of the straight chain amine complexes there is evidence that photo-oxidation of the complex can occur, but it is slow compared to the direct reaction with oxygen.

In some experiments in which the oxidative degradation of the n-butylamine complexes was followed by i.r. spectroscopy a band at 1664 cm^{-1} was observed. This was probably due to small amounts of $Pr^nCH = O$ formed from a intermediate imine, $Pr^nCH=NH$ by reaction with water.

Analytical data, and other criteria of purity, are gathered into Table I and II. All analyses were carried out at I.C.I. (Organic) Division Ltd.

Physical Measurements

U.V. spectra were recorded with Unicam SP 800 (solutions) and SP 700 (solids) spectrometers. The diffuse reflectance spectra were measured against a magnesium oxide blank using the SP 735 attachment. I.r. spectra were recorded for polycrystalline speciment as nujol mulls with a Perkin Elmer 225 instrument in the range 4000-200 cm^{-1}. Conductivity measurements were made for 10^{-3} *M* solutions of complex in distilled water using a Wayne-Kerr bridge.

Results and Discussion

Benzonitrilopentakis(amine)ruthenium(II) Complexes. These complexes were, with the exception of the methylamine compound for which an indirect route was devised, relatively easy to prepare and were indefinitely stable in the solid state. The u.v. spectra of some new benzonitrilepentakis(amine)ruthenium(II) complexes are shown in Table III. The great similarity of the spectra of these freshly prepared solutions, both with respect to band position and band intensity, to that of benzonitrilepentakisammineruthenium(II) salts,[6] together with conductivity and analytical data (Table II) serve to characterise the complexes. On being left the u.v. spectra of the so-

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(10) For details of the apparatus see J.D. Miller and F.D. Oliver, *J.C.S. Dalton*, 2473 (1972).

Table II. Analytical Data for Benzonitrilepentakis(amine)ruthenium(II) Complexes.

Complex	Calculated % C	% H	% N	% X	Found % C	% H	% N	% X	Λ_M ($10^{-3}M$ solns.)[a]	ν(CN) cm^{-1}
$[Ru(MeNH_2)_5(NCPh)]I_2$	23.5	4.9	13.7	41.4	24.1	5.1	13.5	37.9		2184
$[Ru(Pr^nNH_2)_5(NCPh)]Br_2$	40.0	7.6	12.7	24.3	38.6	7.7	12.6	25.1	210	2160
$[Ru(Bu^nNH_2)_5(NCPh)]Cl_2$	50.6	9.4	13.1	11.1	49.6	9.3	13.3	11.3	208	2161
$[Ru(Bu^nNH_2)_5(NCPh)]Br_2$	44.4	8.2	11.5	21.9	43.5	7.9	11.5	22.1	—	2161
$[Ru(Bu^nNH_2)_5(NCPh)]I_2$	39.4	7.3	10.2	30.9	39.4	7.3	10.3	30.4	—	2172
$[Ru(Bn^nNH_2)_5(NCPh)](BF_4)_2$	43.6	8.0	11.3	—	42.4	7.8	11.5	—	—	2175
$[Ru(Bu^iNH_2)_5(NCPh)]Cl_2$	50.6	9.4	13.1	11.1	48.8	8.9	12.9	11.2	230	—
$[Ru(Bu^iNH_2)_5(NCPh)]Br_2$	44.4	8.2	11.5	21.9	41.8	7.4	10.8	21.2	—	—
$[Ru(Bu^iNH_2)_5(NCPh)]I_2$	39.4	7.3	10.2	30.9	39.2	7.4	10.2	30.2	—	2172
$[Ru(Am^iNH_2)_5(NCPh)]Br_2$	48.0	8.8	10.5	20.0	46.8	8.6	10.1	19.1	216	2168

[a] $10^{-3}M$ $[Ni(en)_3]$ $(NCS)_2$ gives Λ_M = 226.

Table III. Ultra-violet spectra of benzonitrile pentakis (amine) complexes of Ruthenium(II).

Complex	Solution spectrum (ethanol)— nm[a]	Diffuse reflectance spectrum (nm and kK)[b]
$[Ru(Pr^nNH_2)_5(NCPh)]Br_2$	226 (4.16)[c], 250 (4.21), 375 (3.99)	415 (24.1), 459 (21.8) sh.
$[Ru(Bu^nNH_2)_5(NCPh)]Cl_2$	228 (4.1), 252 (4.11), 378 (3.88)	422 (23.7), 483 (20.7) sh.
$[Ru(Bu^nNH_2)_5(NCPh)]Br_2$	—	415 (24.1), 471 (21.2) sh.
$[Ru(Bu^iNH_2)_5(NCPh)]Cl_2$	—	402 (24.9), 459 (21.8) sh
$[Ru(Bu^iNH_2)_5(NCPh)]Br_2$	227 (4.13), 255 (4.12), 382 (3.99)	408 (24.5), unresolved sh. 22.5 kK
$[Ru(Am^iNH_2)_5(NCPh)]Br_2$	227 (4.06), 256 (4.03), 388 (3.98)	413 (24.21), 472 (21.2) sh.
$[Ru(NH_3)_5(NCPh)]^{2+}$[e]	227 (4.1), 256 (4.08), 376 (3.93)[d]	—

[a] spectrum of freshly prepared solution. [b] peak positions quoted in nanometers and kilokaysers - only peaks below 30.0 kK. [c] $\log_{10}\varepsilon$ where ε is the apparent extinction coefft. [d] in water; [e] reference 3.

lutions changed and bands characteristic of free benzonitrile developed. A parallel study of the i.r. spectra of more concentrated solutions showed the disappearance of ν(CN) due to co-ordinated benzonitrile and the growth of a new band due to free benzonitrile. The resulting solutions were oxygen sensitive.

The pKa values of the higher amines are relatively insensitive to chain length beyond three carbon atoms[11,12] (e.g. Pr^nNH_2, 10.53; Bu^nNH_2, 10.59; Bu^iNH_2, 10.56) but are larger than that of ammonia (9.21). Since we may assume amines to be σ-bonding ligands, substitutions of amine for ammonia should increase the π-basicity of ruthenium(II) relative to benzonitrile. It has recently been demonstrated[13,14] that ν(CN) in nitrilepentakisammineruthenium(II) salts is a function of the counter anion and that, in particular, ν(CN) increases as the radius of the anion increases. It has been argued[13,14] that interaction between the counter ion and the ammine is the major cause of the variation ν(CN). This point is illustrated by the amines discussed here, thus methylamine, the strongest base of the amines considered, is not much more effective in lowering ν(CN) for benzonitrile than is ammonia (Table II). The major contribution to change of ν(CN) arises from change of anion rather than from change of other coordinated ligands.

The data for the higher amines (Table II) show that the variation of ν(CN) in $RuL_5(NCPh)X_2$ is no greater for different L with fixed X than for given L (n-butylamine) and different anions, X. Even for this C_4 amine the major NH_2 vibrations are clearly sensitive to change of anion with the spectra becoming sharper and better resolved as the size of X increases. Even if we assume that relative pKa values and relative magnitudes of cation-anion interaction will primarily determine the difference in ν(CN) for corresponding complexes of, say, ammonia and n-butylamine, we cannot assume that magnitude of the cation-anion interactions will be the same in the two cases. Thus we cannot meaningfully attribute any observed differences in ν(CN) to the pKa effect alone. It does however appear legitimate to conclude that a genuinely greater (20 cm^{-1}) reduction of ν(CN) for co-ordinated benzonitrile is achieved in the higher amine complexes, in contrast to methylamine, compared with corresponding ammonia complexes. This possibly reflects a relative diminution of the importance of the anion effect as the amine carbon chain length increases.

Hexakis(amine)ruthenium(II) Complexes - I.r. spectra. In Table IV we present some representative i.r. spectra for various hexakis(amine)ruthenium(II) complexes. It is again noted that bands arising from vibrations of the NH_2 group are sensitive to the counter ion such that ν(NH_2) increases and ρ(NH_2) decreases in frequency as the strength of the cation-anion interaction diminishes i.e. as the radius of the anion increases. The results thus parallel those for the benzonitrile complexes (vide supra) and for hexakisamminecobalt(III) salts.[15] It is also noted that i.r. spectra of tris ethylenediamine complexes of ruthenium(II) are sensitive to the nature of the counte-

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Table IV. The i.r. spectra of some hexakis (amine) ruthenium(II) complexes.

Amine Counter-anion	$MeNH_2$ BF_4^-	$MeNH_2$ I^-	$MeNH_2$ Br^-	Pr^nNH_2 I^-	Bu^nNH_2 BF_4^-	Bu^nNH_2 I^-	Bu^nNH_2 Br^-	Bu^nNH_2 Cl^-
$\nu(NH_2)$	3322s 3304s	3216s 3149s	3230s 3158s	3250m 3198s 3160s 3129s	3340s 3305m	3230s 3190s 3123s	3245s 3205s 3125s	3255s 3209s 3120s
$\delta(NH_2)$	1610m	1602s	1603s	1602m 1575s	1648m 1600s	1620s 1590s 1570s	1620s 1590s 1570s	1635s 1597s 1570s
$\rho(NH_2)$	653m	664 669 m	686s	641s	645m	670s 652sh. 640s	668s	678s
ν(Ru-N)	355w		414m-w	395m.w	352w.m	355m	352sh 341m.w	354sh. 342m.w
δ(NRuN) and other modes	242m.s[a]	284m 263s, sh 244s,br	303m.s 295s 268sh 260s 239s	294s 243s	287 br. 254w,sh 235m	280 220 v.b.	298w,sh 278s 262s 242s	301sh 285s 260br 240br

[a] Very broad band with significant absorption from 287 cm^{-1} to definite peak at 242 cm^{-1}.

rion.[16] It is also seen from Table IV that the complexity of some spectra increases with change of anion, the generally more simple spectrum of tetrafluoroborate and iodide salts in the lower frequency region is particularly noticeable. This means that the site symmetry of the cations is not constant across a series of salts.

The assignment of the ruthenium-amine stretching frequencies is of some interest. Metal-ammonia stretching frequencies are often of weak intensity in the i.r. but assignments are now reasonably well established in a number of cases.[17] For $Ru(NH_3)_6^{2+}$, Fairey and Irving[18] assign a band at 437 cm^{-1} to ν_3(Ru-NH$_3$), F$_1$ a suggestion which is reasonable in the light of recent work by Kettle et al. with $Ru(NH_3)_5(N_2)^{2+}$ salts.[19] One of the more definitive studies of metal-ammine complexes[20] establishes that ν_3(M-NH$_2$) is relatively insensitive to the mass of M when M is a heavy metal e.g. M = Co^{3+}, 476 cm^{-1}; M = Rh^{3+}, 472 cm^{-1}; M = Ir^{3+}, 475 cm^{-1}. However the frequency is sensitive to the mass of the ligand e.g. replacement of NH$_3$ by ^{15}NH$_3$[20] or ND$_3$.[19,20] In the case of amine ligands considered here we deal with stronger σ-donor, but heavier ligands; it does therefore seem reasonable to expect the ruthenium-nitrogen vibrations between 400 cm^{-1} and 300 cm^{-1} and the suggested assignments in the table follow.

We have suggested that the rather complex spectra below 300 cm^{-1}, which do not change greatly with the amine, include the expected metal-ligand deformation vibrations.

Electronic Spectra. We tabulate the diffuse reflectance spectra of some hexakis(amine)ruthenium(II) compounds in Table V. The spectra of the methylamine and n-butylamine complexes are very similar to those reported for solutions of $Ru(NH_3)_6^{2+}$ by various workers.[21,22] The very weak feature at 18.2 kK in the spectrum of $[Ru(NH_2Me)_6]Br_2$ may arise from the spin forbidden transition ($^3T_{2g}$) and the bands at 25.6 kK (NH$_2$Me) and 27.4 kK (NH$_2{}^n$Bu) may be assigned to the first spin allowed band i.e. $^1A_{1g} \leftrightarrow {}^1T_{1g}$. The assignment of the bands close to 37 kK must be less certain. The similar band in the spectrum of the hexa-ammine is unlikely to be the second d$\leftrightarrow$d transition since this would require an unrealistic value for the Racah parameter B.[22] Mayer and Taube have assumed that it is a charge transfer band.[21] The spectra of the ethylamine and n-propylamine compounds below 30 kK are similar to those of some hexakisaniline derivatives of ruthenium(II) recently reported by Larkworthy et al.[23] who assigned the two major discernable features below 30 kK to the first two spin allowed bands. However the spectra of tris ethylenediamine and *tris* propylenediamineruthenium(II) complexes suggest that the $^1A_{1g} \leftrightarrow T_{2g}$ band is expected close to 33 kK.[22] We feel that an alternative explanation for our data fo rthe ethylamine and n-propylamine complexes, where a lower frequency shoulder is resolved on the 27 kK, is that the spin forbidden transition is close to the $^1A_{1g} \leftrightarrow {}^1T_{1g}$ transition and has stolen intensity.

The spectrum of the *iso*-butylamine complex in Table V is different in that the feature at 16.5 kK is a prominent one. Analytical data for this unstable compound indicate that it is probably an aquopentakis(iso-butylamine)ruthenium(II) complex. Addition of bromide or iodide ions to the reaction mixture (see experimental section) afforded complexes which analysis suggests to be hexakis(amine) complexes with water of crystallisation. These compounds are also very reactive and the *iso*-butylamine series is the least well characterised of those we report here.

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Table V. Electronic spectra of some ruthenium(II) - amine complexes.

Complex	Diffuse reflectance spectrum in nm (and kilokaysers)
$[Ru(MeNH_2)_6]Br_2$	550(18.2) v.v.w., 391(25.6), 267(37.5)
$[Ru(EtNH_2)_6]I_2$ *	463(21.6) sh., 372 (26.9)
$[Ru(Pr^nNH_2)_6]I_2$ *	455(22.0) sh., 375 (26.7)
$[Ru(Bu^nNH_2)_6]Cl_2$	365 (27.4),[a] 270 (37.0)
$[Ru(Bu^iNH_2)_5(H_2O)]Cl_2$ *	606 (16.5), 377 (26.5)[a]

[a] broad bands, asymmetric to low wave number. * below 30.0kK only.

Oxidative Degradation of Amine Complexes of Ruthenium(II). We present evidence in the experimental section that the hexakis(amine)ruthenium(II) complexes undergo reaction with dioxygen under ambient conditions. The presence of an α-methylene group is necessary for this degradation to occur and in this respect we note that Larkworthy et al.[23] did not report similar reactions for their hexakis(aniline)ruthenium (II) complexes. The methylamine complexes degrade cleanly[6] and the reaction may be studied quantitatively. Thus we have established that 3.25 mole of dioxygen is consumed per mole of $Ru(MeNH_2)_6^{2+}$ and that the products of the reaction include water, methylammonium ions and and insoluble ruthenium(III) cyanide. We have not rigorously excluded the possibility that the material contains ruthenium to hydrogen bonds derived from the hydrogen atoms of the methyl group but we consider this to be improbable in face of the considerable evidence for the cyano-complex. The material is diamagnetic indicating strong antiferromagnetic interactions between the Ru^{3+} ions, probably by bridging cyano-groups a structural feature which would account for the extreme insolubility of the substance. The stability of this compound probably provides the thermodynamic driving force for the reaction. We find that the overall stoichiometry for the reaction is that given in (1).

$$Ru(MeNH_2)_6Br_2+3.25O_2\rightarrow Ru(CN)_3\,.\,3H_2O+2MeNH_3Br+MeNH_3OH+2.5H_2O \qquad (1)$$

Although these reactions do not lend themselves readily to quantitative study, they provide novel and interesting examples of the metal assisted oxidation, by molecular oxygen, of a saturated organic substrate.

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