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(36) However, it must be pointed out that the difference in sensitivity between the two types of systems is less than that claimed.[6] Thus, for the DMPB system at 0.40 and 1.0 M CF_3COOH, $k_{et} = 5.5 \times 10^{-3}$ and 6.1×10^{-3} s^{-1}, respectively. Under the same conditions, values of k_{et} for the BPA system are 1.18×10^{-3} and 1.32×10^{-3} s^{-1}, respectively.

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Synthesis and Properties of π-Bonded Olefin and Acetylene Complexes of Ruthenium(II). Crystal and Molecular Structure of the Pentaammineruthenium(II) Fumaric Acid Complex, $[(NH_3)_5Ru(C_4H_4O_4)]S_2O_6{\cdot}2H_2O$

H. Lehmann,[1a] K. J. Schenk,[1b] G. Chapuis,[1b] and A. Ludi*[1a]

Contribution from the Institut für Anorganische Chemie, Universität Bern, CH-3000 Bern 9, Switzerland, and the Institut de Cristallographie, Université de Lausanne, CH-1015 Lausanne, Switzerland.

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Abstract: Alkenes and alkynes react with the pentaamminemonoaquoruthenium(II) ion to form complexes containing the π-bonded unsaturated organic molecule as a ligand. Syntheses and spectroscopic properties of the complexes with ethylene, isobutene, 1,4-cyclohexadiene, fumaric acid, acetylene, phenylacetylene, and 3-hexyne are reported. The electronic spectra are dominated by an intense band at about 220 nm ascribed to a $\pi(d) \rightarrow \pi^*(L)$ charge transfer. The coordination of the multiple bond to ruthenium is demonstrated by a shift of the C=C and C≡C stretching frequencies by 100-200 cm^{-1} to lower energies. ^1H NMR spectra are consistent with an edge-on bonding arrangement. Formal reduction potentials obtained by cyclic voltammetry are between 0.6 and 1.40 V (vs. NHE) showing the stabilization of the divalent state of ruthenium by the strong backbonding to the ligand. The crystal and molecular structure of the particular case of the fumaric acid complex has been determined by a single-crystal X-ray study to $R = 0.034$ and $R_w = 0.040$ for 1242 unique reflections. The compound crystallizes in the orthorhombic system with four molecules in space group $D_2{}^5$-$C222_1$. Cell dimensions are $a = 9.840$ (3), $b = 10.887$ (4), $c = 15.970$ (4) Å. The five Ru-N distances are between 2.143 (6) and 2.154 (5) Å, the two equivalent Ru-C distances are 2.172 (6) Å, and the C-C bond length of the olefinic group is 1.413 (8) Å.

Introduction

A prominent feature of the pentaammineruthenium(II) moiety is its pronounced affinity for π acids such as pyridine and its many derivatives, nitriles, and sulfur-containing molecules. The bonding and the stability of the resulting complexes have been rationalized in terms of the strong π-back-bonding tendency of the low-spin $t_{2g}{}^6$ configuration of octahedrally or pseudooctahedrally coordinated ruthenium(II).[2] Inasmuch as these molecules play an important role in the chemistry of organometallic compounds, it is surprising that this concept has not been extended to include also π acceptors represented by alkenes and alkynes bonded to $Ru(NH_3)_5$. In the case of known olefin complexes of ruthenium the central metal is in low oxidation states and the other ligands are themselves strong π acids, e.g., CO.[3] Some reactions of a few unsaturated hydrocarbons with pentaammineruthenium(II) have been described in a Ph.D. thesis[4] and a few properties of the corresponding complexes have been reported recently in a preliminary publication.[5] It is remarkable that the formation of these complexes proceeds by a very facile substitution of the water molecule of $Ru(NH_3)_5H_2O^{2+}$ by an alkene or alkyne. Complexes $Ru(NH_3)_5L^{2+}$ (L = alkene, alkyne) described in this paper represent a link between classical coordination compounds and organometallic chemistry in much the same way as the well-known Zeise salt, $Cl_3PtC_2H_4{}^-$. We have studied the reaction of $Ru(NH_3)_5H_2O^{2+}$ with a variety of unsaturated organic molecules in water and acetone as solvents. Some representative examples are described in this report which also comprises the crystal and molecular structure of one particular case, namely, of the complex with fumaric acid. The structures of a number of transition-metal compounds containing olefins in the presence of other π acids have been recently reviewed.[6] No structure, however, appears to have been determined of complexes of the pentaammineruthenium(II) moiety and an alkene representing the sixth ligand.

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Experimental Section

Preparations and Analytical Data. All the synthetic procedures were carried out in an argon atmosphere using Schlenk-type glassware.[7] Reagents of the highest purity available were purchased from Merck, Fluka, or Aldrich, $Ru(NH_3)_6Cl_3$ from Johnson-Matthey. Doubly distilled water was used as a solvent in the spectroscopic and electrochemical measurements.

$[Ru(NH_3)_5H_2O]S_2O_6$. $[Ru(NH_3)_5Cl]Cl_2$[8] (2.12 g) in 25 mL of H_2O was treated with 3.2 g of $AgCF_3COO$ dissolved in 5 mL of H_2O at 40 °C until all of the AgCl had coagulated. Argon was bubbled through the filtrate for 1 h. The solution was transferred to a Schlenk vessel containing a glass frit with 3 g of amalgamated Zn and kept over the Zn for 0.5 h. After filtration a solution of $Na_2S_2O_6{\cdot}2H_2O$ in 20 mL of H_2O was added. After standing overnight in an ice bath the crystalline precipitate was isolated by filtration, washed with methanol and ether, and dried in vacuo. The solid $[Ru(NH_3)_5H_2O]S_2O_6$ was kept under argon at −18 °C without decomposition for months.

Since all the complexes with alkenes and alkynes were prepared the same way only two syntheses are described as representative examples.

$[Ru(NH_3)_5C_4H_4O_4]S_2O_6{\cdot}2H_2O$. A saturated solution of $C_4H_4O_4$ (fumaric acid) in 30 mL of H_2O was degassed with argon. Addition of 40.7 mg of $[Ru(NH_3)_5H_2O]S_2O_6$ produced an intense yellow solution which was cooled to 0 °C. Needle-shaped, yellow crystals of approximately 1 mm length were isolated after 2 days, washed with methanol and ether, and dried in vacuo, yield 51%.

$[Ru(NH_3)_5C_2H_2]S_2O_6$. C_2H_2 was bubbled at 40 °C through a solution containing freshly prepared $Ru(NH_3)_5H_2O^{2+}$ (from 500 mg of $[Ru(NH_3)_5Cl]Cl_2$). Within a few minutes the yellow solution turned brown. After 30 min of C_2H_2 bubbling the solution was transferred through a G4 frit into another Schlenk vessel containing a solution of 1 g of $Na_2S_2O_6{\cdot}2H_2O$ in 5 mL of H_2O. The brown, microcrystalline solid was filtered after 2 h, washed with ice-cold water, methanol, and ether, and dried in vacuo, yield 38%. The PF_6^- salts used for measuring ^1H NMR spectra and for some electrochemical experiments were prepared in an analogous way using $[Ru(NH_3)_5H_2O](PF_6)_2$ as the starting complex. Replacement of NH_3 by ND_3 was achieved by recrystallizing $[Ru(NH_3)_5Cl]Cl_2$ twice from D_2O and carrying out the reduction in the presence of the organic ligand in D_2O-DCl.

Analyses. Ru was determined colorimetrically.[9] C, H, N, and S analyses were performed by the analytical laboratory of Ciba-Geigy, Basel, Switzerland. Analytical data are available as supplementary material.

Physical Measurements. UV-vis spectra of the aqueous solutions of the complexes were recorded on a Cary 17. Since all the solutions are air sensitive they were kept under argon for the measurements. A Perkin-Elmer IR-580 was used for measuring the infrared spectra in the range of 4000-180 cm^{-1}. The samples were prepared either as Nujol mulls or as KBr (CsI) pellets. ^1H NMR spectra were recorded on a Varian XL-100 or a Bruker WP-80 using either D_2O or acetone-d_6 as a solvent. All the ^1H NMR data in this paper are referred to the signal of tetramethylsilane (Me_4Si) as zero point. A conventional three-electrode setup (working electrode, Pt foil of 3.4 cm^2; reference electrode, Ag electrode in acetonitrile, SSCE in aqueous solution) was used for cyclic voltammetry. Supporting electrolytes were either 0.1 M $[(n\text{-}Bu)_4N]PF_6$ in acetonitrile or a 0.1 M KCl-0.001 M HCl aqueous solution. The following couples served as calibrating standards: $Ru(bpy)_3^{3+/2+}$ (1.26 V),[10] $Fe(bpy)_3^{3+/2+}$ (1.05 V),[10] and $Ru(NH_3)_6^{3+/2+}$ (0.05 V).[11]

Collection of Diffraction Data. Crystals of the title compound from the synthesis described above were yolk yellow and had rough faces, a feature possibly due to the loss of water at the surface. Most of them displayed {111} sphenoids and {110} prisms. The measured specimen was even along the *a* and *b* cell edges but twice as extended along the *c* axis; its volume was 1.86 × 10^{-4} mm^3. An absorption correction yielded transmission factors between 0.888 and 0.925. Lattice constants were obtained from a least-squares optimization of 16 accurately centered reflections (2θ(Mo $K\alpha$) between 17 and 18°). The density at 20 °C was determined by flotation in bromoform/bromobenzene; it agrees acceptably with four formula units per cell. Relevant data of the crystal are listed in Table I.

Single crystal intensities were collected on a Syntex $P2_1$ automatic diffractometer equipped with a molybdenum tube ($K\bar{\alpha}$ = 0.710 69 Å). Unwanted radiation was eliminated by a niobium filter. A range of 1° was scanned on each side of the $K\alpha_1/K\alpha_2$ doublet; at each end of this interval stationary background was measured during 25% of the scan time. The scan speed varied between 2 and 10°/min depending on the intensity of the reflection. Analysis of the profiles was done by a modified Lehmann-Larson algorithm.[12]

Table I. Crystal Data for $[Ru(NH_3)_5(HOOCCH{=}CHCOOH]$-$S_2O_6{\cdot}2H_2O$

a = 9.840 (3) Å	$F(000)$	= 1016
b = 10.887 (4) Å	space group	= $D_2^5-C222_1$
c = 15.970 (4) Å	ρ_{meas}	= 1.923 (4) g cm^{-3}
V = 1711 (1) $Å^3$	ρ_{calcd}	= 1.935 (1) g cm^{-3}
Z = 4	μ(Mo $K\bar{\alpha}$)	= 12.0 cm^{-1}

For the reduction of the data and the determination of the structure the XRAY-72 system of programs[13] was used. Drawings were plotted by means of the ORTEP program.[14] Neutral scattering factors[15] were chosen and anomalous dispersion corrections[16] were applied for ruthenium and sulfur atoms.

Extinctions from a precession photograph (*hkl*, $h + k = 2n$; 00*l*, $l = 2n$) and the distribution of the normalized structure factors revealed the space group symmetry as $C222_1$. At 21 °C 1242 unique reflections were collected up to $\sin\theta/\lambda = 0.673$. For all of them two or more equivalent intensities were available; their reliability factor was $R_i = 0.027$. Three check reflections were recorded after each 57 intensities. They remained moderately stable (within 10%). The variances $\sigma^2(I)$ estimated from counting statistics had to be augmented by 0.000 465 times the intensity in order to account for these fluctuations; 1101 of the unique reflections had an intensity larger than $3\sigma(I)$. Weights assigned were $w(F) = 1/\sigma^2(F)$.

Solution and Refinement of the Structure. The positions of Ru, S, and three N atoms were obtained from a Patterson map. A F_o synthesis phased with these atoms revealed in turn the remaining atoms of the cation. After a few cycles of isotropic refinement and subsequent ΔF syntheses, the rest of the nonhydrogen atoms could be located. After a final anisotropic full-matrix refinement—the number of reflections per parameter being optimized was 10.7—no shift was larger than 0.025 times the standard deviation estimated for the refined parameter (average shift/error = 0.003). A ΔF synthesis showed no peak to be higher than 0.7 e $Å^{-3}$. Moreover, the most prominent residuals are in the neighborhoods of either the heavy atoms or the hydrogen-bearing atoms. No attempt, however, was made to locate the hydrogen atoms.

The temperature factors of the dithionate atoms are especially large (the largest mean square amplitudes lie between 0.107 and 0.298 $Å^2$). We could not find any satisfying model of thermal motion explaining such monstrous temperature ellipsoids. Thus we suspected that a positionally disordered structure might account for the uncertainty in the dithionate positions. We divided these atoms along the most prominent axis of their thermal ellipsoids and performed an isotropic least-squares refinement, keeping the atoms of the complex and the water molecules invariant. This model converged smoothly to an R value of 0.036. The temperature factors were more reasonable (between 0.03 and 0.09 $Å^2$), but the geometry of the dithionates became more distorted than in the unsplit model (S-O, 1.36-1.54 Å; S-S-O, 97-112°; O-S-O, 105-122°; the S-S distance of 2.12 Å only was somewhat better).

The final residuals are R = 0.034, R_w = 0.040, and the goodness of fit = $\{\sum w(\Delta F)^2/\text{number of reflections} - \text{number of parameters}\}^{1/2}$ = 2.95. The final parameters are given in Table II. Structure factor tables are available as supplementary material.

Results and Discussion

UV-Visible Spectra. All the alkene and alkyne complexes of pentaammineruthenium(II) investigated in this study were obtained as crystalline or microcrystalline samples of a light yellow to brown color. The spectra (Figure 1) have to be discussed in terms of the following three electronic transitions: (1) Owing to their high energy, well below 180 nm, it is quite unlikely that intraligand absorption due to $\pi \rightarrow \pi^*$ transitions will be observed in the accessible spectral region. These transitions will only be observable if the organic molecule contains an aryl or related group as in phenylacetylene. (2) Weak bands at about 400 nm in the spectra of various substituted pentaammineruthenium(II) complexes have been assigned to li-

Table II. Positional ($\times 10^4$) and Thermal Parameters ($\times 10^3$) for $[Ru(NH_3)_5(HOOCCH{=}CHCOOH)]S_2O_6 \cdot 2H_2O$[a]

atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	0	944.3 (5)	−2500	23.4 (3)	20.7 (3)	17.2 (2)	0	3.3 (5)	0.1
S	1059 (3)	4774 (2)	−639 (1)	81 (2)	40 (1)	52 (1)	−16 (1)	31 (1)	−14 (1)
N (1)	−496 (5)	1225 (5)	−1200 (3)	40 (3)	29 (3)	21 (2)	1 (2)	7 (2)	−1 (2)
N (2)	2151 (5)	1042 (5)	−2271 (3)	27 (3)	43 (3)	34 (3)	−2 (3)	−2 (2)	7 (3)
N (3)	0	2913 (6)	−2500	45 (4)	22 (3)	33 (3)	0.8	14 (7)	−0.2
O (1)[b]	−829 (5)	−1172 (5)	−4269 (3)	57 (3)	58 (4)	30 (2)	−17 (3)	6 (2)	−2 (3)
O (2)[b]	−2218 (5)	−1595 (4)	−3212 (3)	40 (3)	41 (3)	42 (3)	−8 (3)	2 (2)	−4 (2)
O (3)[c]	−36 (9)	3938 (6)	−712 (4)	134 (6)	101 (6)	68 (4)	−75 (7)	25 (5)	−39 (4)
O (4)[c]	−2318 (9)	4156 (8)	−771 (6)	127 (8)	85 (6)	20 (1)	12 (6)	131 (7)	−14 (7)
O (5)[c]	990 (10)	5889 (7)	−1090 (4)	22 (1)	69 (5)	67 (5)	−13 (6)	11 (6)	24 (4)
O (6)[d]	−2679 (5)	1743 (5)	−4617 (4)	46 (4)	69 (4)	41 (3)	0 (3)	−3 (2)	−6 (3)
C (1)	−1099 (8)	−1267 (6)	−3465 (4)	38 (4)	20 (3)	34 (3)	−6 (3)	3 (3)	1 (3)
C (2)	110 (10)	−942 (5)	−2938 (3)	29 (3)	24 (2)	31 (2)	−4 (5)	1 (4)	2 (2)

[a] The temperature factor has the form $\exp(-T)$, where $T = 2\pi^2\Sigma_{ij}h_ih_jU_{ij}a_i^*a_j^*$; a_i^* and a_j^* are reciprocal cell constants. [b] Fumaric acid. [c] Dithionate anion. [d] H_2O molecule.

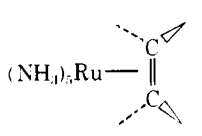
Table III. Electronic Spectra of $Ru(NH_3)_5$-Alkene and -Alkyne Complexes[a]

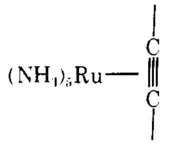
L	absorption max, λ_{max}, nm
H_2O[b]	416 (1.6), 310 sh, 268 (2.8)
N_2[c]	221 (4.2)
CH_3CN[d]	350 (2.4) 229 (4.2)
C_2H_4	385 (2.5), 270 sh, 217 (3.3)
C_4H_8 (1-butene)	385 (1.6), 275 sh, 224 (3.2)
(C_4H_8) (isobutene)	390 (1.7), 315 sh, 237 (3.2)
C_6H_8 (1,4-cyclohexadiene)	233 (3.2)
$C_4H_4O_4$ (fumaric acid)	362 (2.2) 252 (3.7)
$C_4H_3O_4^-$ (maleic acid monoanion)	360 (2.2) 252 (3.6)
C_2H_2	385 (2.3), 280 sh, 219 (3.3)
C_8H_6 (phenylacetylene)	435 (2.2), 255 (3.8), 229 (4.0), 203 (3.9)
C_6H_{10} (3-hexyne)	300 sh, 260 sh, 210 (3.5)

[a] Values of log ε in parentheses; sh denotes a shoulder. [b] Reference 17. [c] I. M. Treitel, Ph.D. Thesis, California Institute of Technology, 1971. [d] Reference 18.

gand field transitions.[17] (3) Intense bands in the ultraviolet region of pentaammineruthenium(II) complexes with N_2 or CH_3CN have been attributed to a $d\pi(\text{metal}) \rightarrow \pi^*(\text{ligand})$ charge transfer.[18]

The data of Table III show that the electronic spectra of the various alkene and alkyne complexes follow the same general pattern. The most intense band occurs for all of the compounds between 210 and 250 nm. Moreover, an analogy to the spectra of pentaammineruthenium(II) complexes with the π acids N_2 and CH_3CN is observed. Whereas an "end-on" bonding geometry is realized for the latter ligands, all the experimental evidence (cf. following sections) is consistent with an "edge-on" arrangement for the alkene and alkyne complexes, as in the Zeise salt. The electronic structure of our complexes can





therefore be discussed qualitatively in terms of the Dewar-Chatt-Duncanson model[19] for π complexes. The appropriate symmetry of the complexes assuming identical substituents at the two carbon atoms joined by a multiple bond is given by the point group C_{2v}. The obvious choice for the z axis is the direction bisecting the double or triple bond. Only the d_{xz} orbital of ruthenium has the correct symmetry (b_1) to interact with the π* orbital of the unsaturated organic ligand in the sense of the back-bonding. The other d orbitals (symmetry a_2 and b_2) are nonbonding within the framework of this approximation. A charge-transfer transition $d \rightarrow \pi^*$ is symmetry allowed for $b_1(xz) \rightarrow b_1(\pi^*)$. According to this simple model the intense band occurring between 210 and 250 nm is thus assigned to this transition. This assignment is supported by the observation that the energy of this absorption increases with decreasing energy of the π* orbital of the free ligand within a homologous series.

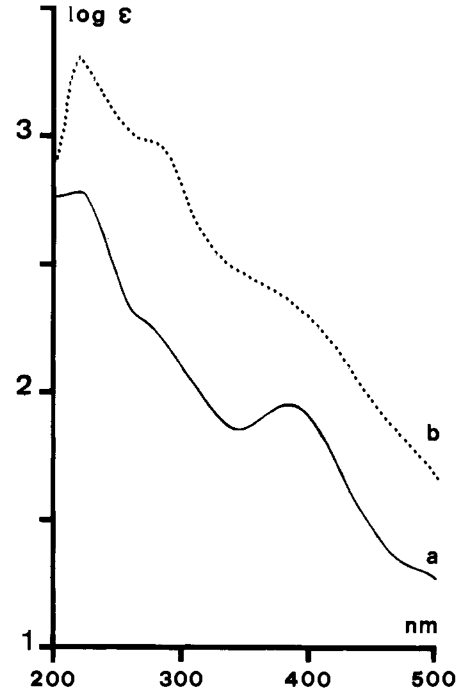


Figure 1. Absorption spectra of $[(NH_3)_5RuC_2H_4]^{2+}$ (a) and $[(NH_3)_5RuC_2H_2]^{2+}$ (b). The spectrum (a) is displaced vertically by −0.5 units of log ε.

Infrared Spectra. A direct demonstration of the back-bonding interaction between metal and ligand is observed in the infrared spectra of the various complexes. All the C=C and C≡C stretching frequencies are shifted toward lower wavenumbers compared to the free ligands. This shift is related to a weakening of the corresponding bonds effected by the transfer of electron density from ruthenium to the π* ligand

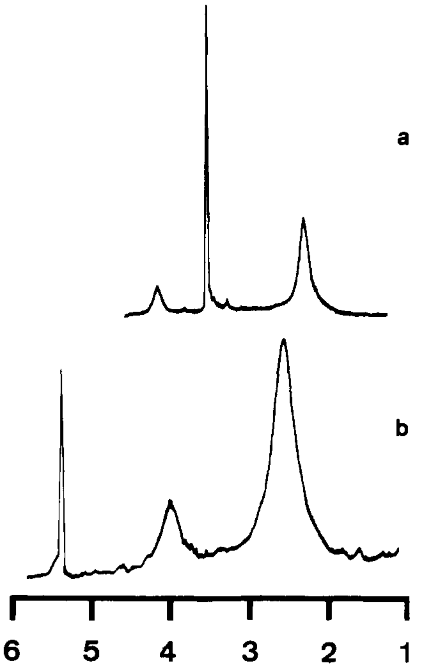


Figure 2. ^{1}H NMR spectra of $[(NH_3)_5RuC_2H_4]^{2+}$ (a) and $[(NH_3)_5RuC_2H_2]^{2+}$ (b).

orbitals. The change in the stretching frequency of the acetylenic and olefinic bond of 100 to 200 cm^{-1} is of the same magnitude as that observed for similar π complexes of Pt(II).[20] A list of these stretching vibrations is presented in Table IV. In some cases the close vicinity of the δ_d NH_3 vibration to the diagnostic C=C modes required a complete replacement of NH_3 by ND_3. In the low-energy range Ru-N stretching vibrations are observed between 400 and 470 cm^{-1} and N-Ru-N deformation modes between 250 and 300 cm^{-1}. Since Ru-C vibrations are expected to occur in the same spectral region no definite assignment of these low-energy bands is made.

^{1}H NMR Spectra. Substitution according to $Ru(NH_3)_5L + S \rightarrow Ru(NH_3)_5S + L$ (S = solvent) takes place in D_2O and acetone-d_6 as well and proceeds to completion within a few hours. In order to reasonably determine the area of the individual signals we always used freshly prepared solutions. Because of the required long scanning periods for ^{13}C NMR spectra these data could not be obtained.

For the prototype of the π complexes, the Zeise salt, the proton signal of C_2H_4 is shifted by 1.12 ppm toward higher field.[21] Again this shift is consistent with the $d \rightarrow \pi^*$ back-bonding description for this class of compounds. The ^{1}H NMR spectra of all of the $Ru(NH_3)_5$ alkene complexes exhibit this typical shift of 1-2 ppm to higher field as a consequence of coordination to ruthenium (see Table V). The opposite shift occurs in the acetylenic complexes, where the proton signals are shifted by 2-3 ppm toward lower field owing to the removal of the axial symmetry of the triple bond by coordination.[22] The displacements observed for the ^{1}H NMR signals for olefin as well as acetylene complexes are in complete agreement with predictions made on the basis of the back-bonding model. The alkene protons are thus shifted toward the signal of the corresponding alkane, the alkyne protons toward the corresponding alkene. Two representative spectra are shown in Figure 2. The signals of various substituents of the organic molecule are not significantly affected by coordination.

The ammonia protons of the $Ru(NH_3)_5$ moiety appear as rather broad signals at 2-3 ppm for the cis ammonias and at 3-4 ppm for the ammonia molecule trans to the organic ligand. A clear distinction of the ^{1}H NMR signals for the cis and trans ammonia ligands has been published recently.[23] The proton signals of the cis ammonias appear in a rather narrow range from 2.3 to 2.7 ppm. On the other hand, the signals of the trans ammonia are scattered more widely and are loosely related to properties of the organic ligand (cf. next section).

Table IV. Stretching Frequencies of the C-C Multiple Bonds in Alkene and Alkyne Complexes $Ru(NH_3)_5L^{2+}$

L	ν free ligand, cm^{-1}	ν complex, cm^{-1}	$\Delta\nu$, cm^{-1}
C_2H_4	1623 (R)	1541	82
C_4H_8 (isobutene)	1661	1527	134
C_6H_8 (1,4-cyclohexadiene)	1642	1496 1659	146 −17
$C_4H_4O_4$ (fumaric acid)		1525	
C_2H_2	1974	1775	199
C_8H_6 (phenylacetylene)	2119	1890	229
C_6H_{10} (3-hexyne)	2118	1995	123

Electrochemistry. The reduction potentials of the couples $Ru(NH_3)_5L^{3+/2+}$ span a wide range from −0.042 V for L = Cl[24] to +1.46 V for L = $S(CH_3)_3^+$ [23] vs. the normal hydrogen electrode (NHE). It has been pointed out that the increase of the formal potential in the series of ligands reflects the tendency of the ligand to participate in the back-bonding. Good π^* acceptors like pyrazine or N_2 have positive potentials of 0.49 and 1.12 V, respectively.[24]

The formal potentials of the ruthenium(II) pentaammine alkene and alkyne complexes listed in Table VI are obtained from the cyclic voltammograms. The observed peak-to-peak separations of 70-100 mV indicate near-Nernstian behavior of these compounds. It is apparent from these data that Ru(III)/Ru(II) potentials are considerably higher for unsaturated hydrocarbons as ligands than for pyridine and its many derivatives.[24] This stabilization of the divalent state of ruthenium is again attributed to the decrease of electron density at the ruthenium center by back-bonding. Obviously, this effect is enhanced by electron-withdrawing substituents at the olefinic or acetylenic carbon atoms. The ethylene and fumaric acid complexes may serve as prominent examples where the introduction of two carboxylic groups shifts the potential from 0.93 to 1.40 V.

In the preceding section it was pointed out that the ^{1}H NMR signals of the cis ammonia ligands are virtually independent of the nature of the coordinated alkene or alkyne. The signals of the trans ammonia, however, are shifted downfield with increasing back-bonding capacity of the organic ligand, where the reduction potential of the complex serves as an indicator of this property (Figure 3). This deshielding effect on the trans ammonia protons is explained as a consequence of a decrease of the σ-electron density of the $Ru-NH_3$ (trans) bond. It appears from our experimental data that the enhancement of the π-back-bonding Ru-alkene (alkyne) weakens the σ-ligand $\rightarrow$ metal donor interaction for the ligand trans to the alkene (alkyne).

Description of the Structure. The structure, shown in Figure 4, consists of ruthenium complexes and dithionate anions linked by hydrogen bonds via the water molecule. The corresponding O-O distances are between 2.62 and 2.94 Å for three pairs of oxygen atoms. We judge them to be hydrogen bonded according to the criterion of Hamilton and Ibers[25] applied to Bondi's[26] van der Waals radii. The remaining oxygen atoms lie farther apart than 3.20 Å and are thus considered nonbonded. The scheme of the hydrogen bonds is very reasonable:

Table V. ^{1}H NMR Spectra of Alkene and Alkyne Complexes $Ru(NH_3)_5L^{2+}$ [a]

L	cis NH_3	trans NH_3	Δ(trans − cis)	H of L	free L
NH_3	2.55	2.55			
CO[b]	2.6	3.7	1.10		
$(CH_3)_2SO$[b]	2.4	3.6	1.2		
C_2H_4	2.32	4.19	1.87	3.57 (4 H)	5.38
C_4H_8 (isobutene)	2.28	3.97	1.69	1.50 (6 H)	1.72
				3.45 (2 H)	4.65
C_6H_8 (1,4-cyclohexadiene)	2.35	4.23	1.88	5.72 (2 H) 4.04 (2 H)	5.68
				2.63 (4 H)	2.65
$C_4H_4O_4$ (fumaric acid)	2.65	4.75	2.10	4.90 (2 H)	6.66
C_2H_2	2.53	3.98	1.45	5.39	2.88
C_8H_6 (phenylacetylene)	2.58, 3.03	3.97	1.39, 0.94	7.43 (2 H) 7.13 (3 H)	7.37
				4.77 (1 H)	3.08
C_6H_{10} (3-hexyne)	2.40	3.40	1.0	2.10 (6 H)	
				1.60 (4 H)	

[a] Data given in parts per million relative to $\delta(Me_4Si)$ 0. [b] Reference 23.

Table VI. Formal Reduction Potentials of Alkene and Alkyne Complexes $Ru(NH_3)_5L^{3+/2+}$ from Cyclic Voltammograms Measured in 0.1 M KCl/0.001 M HCl

L	*E*, V vs. NHE	L	*E*, V vs. NHE
NH_3	0.05[a]	C_2H_2	0.665
C_2H_4	0.93	C_8H_6 (phenylacetylene)	0.95
C_4H_8 (isobutene)	0.85		
C_6H_8 (1,4-cyclohexadiene)	0.86[b]	C_6H_{10} (3-hexyne)	0.78
$C_4H_4O_4$ (fumaric acid)	1.40[b]		

[a] Reference 24. [b] 0.1 M $[(n\text{-}Bu)_4N]PF_6$ in acetonitrile.

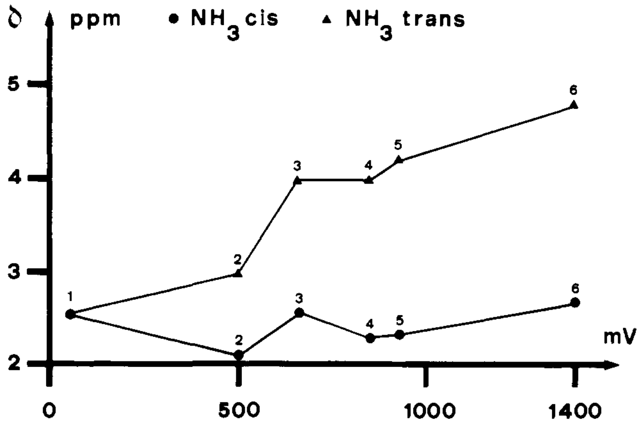


Figure 3. Dependence of the ^{1}H NMR signals of NH_3 from the reduction potential in complexes $[(NH_3)_5RuL]^{2+}$. L: 1, NH_3; 2, $S(CH_3)_2$;[23] 3, C_2H_2; 4, C_4H_8 (isobutene); 5, C_2H_4; 6, $C_4H_4O_4$ (fumaric acid).

all of the acceptor and donor positions of the water molecule and the hydroxy group are saturated. The hydrogen bonds between carboxy group, water, and dithionates form infinite chains along [110] and [1$\bar{1}$0] building up two-dimensional rectangular networks. Nitrogen does not appear to contribute considerably to the hydrogen-bonding scheme, the shortest nitrogen-oxygen distance being 3.08 Å. The geometrical properties of the anion (Table VII) are compatible with data found in other dithionate structures.[27]

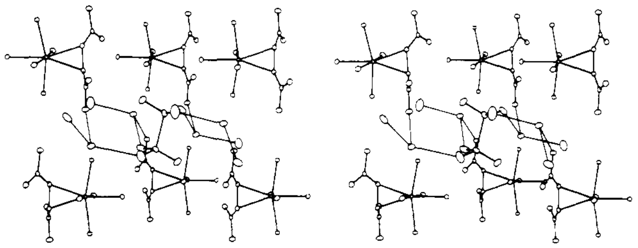


Figure 4. Stereoview of the unit cell of $[Ru(NH_3)_5(HOOCCH{=}CHCOOH)]S_2O_6{\cdot}2H_2O$ along [100].

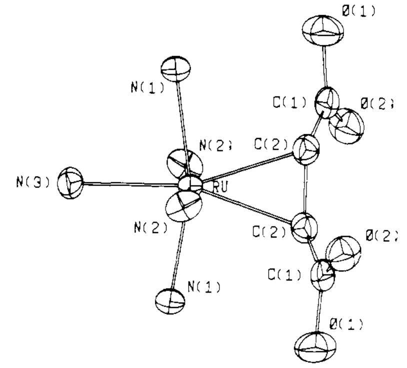


Figure 5. The structure of the $[(NH_3)_5RuHOOCCH{=}CHCOOH]^{2+}$ complex displaying the 50% probability ellipsoids.

The essential part of the crystal structure, the pentaammineruthenium(II)-fumaric acid complex, is depicted in Figure 5. The complex contains a twofold axis imposed by the space group symmetry coinciding with the N3-Ru bond and bisecting the olefinic bond of fumaric acid. All of the equatorial nitrogen atoms are bent umbrella-like away from the fumaric acid molecule, illustrated by the concerned N-Ru-N angles being smaller than 90° (Table VII).

The Ru-N distances of the complex are in quite good agreement with corresponding bond lengths found in other Ru(II) compounds (2.11-2.14 Å).[28] The C2-C2′ bond is practically perpendicular to the plane of the Ru, N2, N2′, and N3 atoms, the tilting angle being only 1(1)°. As a consequence of the coordination the mirror plane of the fumaric acid molecule is lost.[29] Since the position of the olefinic hydrogen atom cannot be determined precisely, the angles α and β defined by Ittel and Ibers[6] cannot be calculated from our structural data. As a measure of the distortion of the four carbon atoms from

Table VII. Selected Distances (Å) and Angles (deg) in $[Ru(NH_3)_5(HOOCCH{=}CHCOOH)]S_2O_6{\cdot}2H_2O$

	Distances		
Ru-N(1)	2.154 (5)	C(2)-C(2)′[a]	1.413 (8)
Ru-N(2)	2.150 (5)	C(1)-C(2)	1.50 (1)
Ru-N(3)	2.143 (6)	C(1)-O(1)	1.315 (8)
Ru-C(2)	2.172 (6)	C(1)-O(2)	1.226 (9)
S-S′	2.098 (3)	S-O(4)	1.426 (9)
S-O(3)	1.416 (9)	S-O(5)	1.414 (8)
O(6)-O(1)	2.620 (7)	O(6)-O(3)	2.94 (1)
O(6)-O(4)	2.72 (1)		
	Angles		
N(1)-Ru-N(2)	93.0 (2)	N(1)-Ru-N(1)′	163.7 (2)
N(1)-Ru-N(3)	81.8 (1)	N(2)-Ru-N(3)	87.2 (2)
N(1)-Ru-N(2)′	86.2 (2)	N(2)-Ru-N(2)′	174.3 (2)
C-Ru-C′	38.0 (2)		
O(1)-C(1)-O(2)	121.7 (6)	C(2)′-C(2)-C(1)	116.1 (8)
S′-S-O(3)	103.4 (3)	O(3)-S-O(4)	110.2 (5)
S′-S-O(4)	104.8 (4)	O(3)-S-O(5)	118.1 (5)
S′-S-O(5)	107.1 (3)	O(4)-S-O(5)	112.0 (6)
O(3)′-O(6)-O(4)′	118.5 (3)	O(1)′-O(6)-O(3)′	93.9 (2)
O(1)′-O(6)-O(4)′	107.0 (4)		

[a] Primed atoms are related to the umprimed ones by a twofold axis.

planarity the torsion angle γ (180° for the planar geometry) can be used.[6] Its value, 150 (2)°, for our complex is almost equal to the same angle (143–154°) determined in the structure of $[Fe(CO)_4(\text{fumaric acid})]$.[6,30] The Ru-C2 distance of 2.172 (6) Å is rather large compared to tabulated values[6] but is still shorter than the corresponding distance in $RuCl_2(CO)(C_2H_4)(PMe_2Ph)_2$, where the Ru-C distance is 2.214 (4) Å.[31] In the latter compound, containing also hexacoordinated Ru(II), the C=C bond is lengthened to 1.376 (10) Å, whereas in the fumaric acid complex this distance is found to be 1.413 (8) Å, significantly longer than the value of 1.348 Å reported for free fumaric acid.[29] This observed lengthening of the olefinic bond is, of course, expected within the framework of the back-bonding model which has been used to rationalize the other properties of these complexes.

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Supplementary Material Available: Analytical data and a listing of structure factors (7 pages). Ordering information is given on any current masthead page.

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