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Ruthenium Ammine Disulfides

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The complex of 1,2-dithiane with pentaammineruthenium(II) can be prepared by direct substitution on the pentaammineaquo ion, but with the analogous five-membered ligand, preparation by this route is not successful. The disulfide complexes can, however, be prepared by starting with $Ru(NH_3)_5OH_2^{2+}$ and 1,4-butanedithiol or 1,3-propanethiol. The products of these substitution reactions undergo one-electron oxidations to the Ru(III)–thiol state and, on further one-electron oxidation, produce the cyclic disulfides coordinated to Ru(II). This can be further oxidized, in a process which in the case of the six-membered ring was shown to be reversible on the cyclic voltammetric time scale (E_f = 630 mV vs. NHE at 25 °C), to the Ru(III) complex. In contrast to a simple thioether complex of Ru(III) which shows ligand to metal charge transfer at ca. 450 nm, the ruthenium(III) disulfide (six-membered ring) has a band at 618 nm with a second band discernible as a shoulder at 360 nm. The splitting is analogous to that observed with 1,5-dithiocane as ligand, which has been ascribed to sulfur lone-pair interactions. As expected on this basis, the splitting observed in the Ru(III) complex of the five-membered disulfide is even greater, owing to the fact that the dihedral angle between the sulfur lone pairs is smaller in the five-membered than in the six-membered ring.

In a previous paper, some manifestations in ligand-to-metal charge-transfer spectra of sulfur lone-pair interactions in the spectra of cyclic dithioether complexes of pentaammineruthenium(III) were described.[1] Such interactions have been well documented in the photoelectron spectra[2] of the ligands themselves, and after the fact at least, their influence on the charge-transfer spectra is not astonishing. The interactions are expected to be particularly prominent in disulfide complexes, and the work to be described was undertaken to investigate the electronic absorption of disulfide complexes of Ru(III). Disulfide complexes of metals are unusual, and since the desired species have not previously been prepared, their synthesis seemed a worthy goal in its own right.

Experimental Section

The procedures for handling air-sensitive solutions made use of argon as a blanketing gas and have been described elsewhere.[3]

Distilled water was further purified by redistilling from alkaline permanganate in an all-glass still. Acetone used as solvent was Baker Analyzed reagent grade.

Cerium(IV) sulfate was commonly used for quantitative oxidations. The salt $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$ was purchased from G. F. Smith and was standardized by using primary-standard grade sodium oxalate.

The ligands 1,2-ethanedithiol, 1,3-propanedithiol, 1,4-butanedithiol, and 1,6-hexanedithiol were purchased from Aldrich and were used without further purification.

Lipoamide (racemic) was purchased from Sigma Chemical Co. and used without further purification. Hydrochloric acid (Baker) was titrated against Titrisol–0.1 N NaOH.

The compound 1,2-dithiane used in the direct synthesis of a disulfide complex was prepared by the procedure of Claeson et al.[4] 1,4-Butanedithiol (21.6 g, 0.171 mol) was dissolved in 2 L of 50% ethanol. A 5% alcoholic iodine solution was then introduced dropwise with stirring until a faint yellow color persisted. A few drops of 1% $Na_2S_2O_3$ in water were then added to decolorize the solution. After the addition of 3 L of water, the mixture was extracted with two 150-mL portions of petroleum ether. The extracts were combined and dried over anhydrous $MgSO_4$. On cooling of the solution to −80 °C, crystals of 1,2-dithiane were deposited, but these rapidly polymerized to a petroleum ether-insoluble rubbery solid when dried. Accordingly, no further purification was attempted, and the ligand was stored as a solution in petroleum ether in the absence of light at −5 °C. Under these conditions, the disulfide is stable for extended periods of time (>1 year).

The compounds $[(NH_3)_5RuXC_6H_5](PF_6)_2$ (X = S, Se), referred to in Table I, were incidental to the main purpose of this investigation, and the method of preparation is described here. Diphenyl disulfide or diphenyl diselenide (220 mg) was dissolved in 5 mL of acetone, and the mixture was degassed in a stream of argon. Solid $[(NH_3)_5RuOH_2](PF_6)_2$ was then added, and within 3 min the mixture had changed from orange to brown to red (sulfur) or orange to green to blue (selenium). After 10 min the product was precipitated by adding the solution to 50 mL of ether. The yield was >95%.

Analyses were not performed on the sulfur derivative, but the quality of the preparation was established by comparing the properties with those of a material made by an alternate procedure, with excellent agreement. In the alternate preparation, benzenethiol reacted with $[(NH_3)_5RuOH_2]^{2+}$ in aqueous solution, and the product was then oxidized by air. Anal. Calcd for $[(NH_3)_5RuSeC_6H_5](PF_6)_2$: C, 11.36; H, 3.34; N, 11.06; Se, 12.47; Ru, 15.97. Found: C, 11.51; H, 3.01; N, 10.54; Se, 12.0; Ru, 15.69.

Results

Preparation of Pentaammine(1,2-dithiane)ruthenium(II) Hexafluorophosphate by Substitution. Synthesis by simple substitution is possible when 1,2-dithiane is the ligand. Owing to the instability of the unsubstituted five-membered analogue,[5] the preparation of the corresponding Ru(II) complex was not undertaken with it. The description of the successful synthesis by substitution follows.

One hundred milligrams of $[(NH_3)_5RuOH_2](PF_6)_2$ was added to approximately a threefold excess of 1,2-dithiane dissolved in petroleum ether and then the mixture was placed in 5 mL of degassed acetone, whereupon the solution turned red over the course of 30 min. The mixture was then added to an equal volume of 0.2 M HCl and loaded on a column containing Dowex 50W-X2 ion-exchange resin (acid form), and a yellow product was eluted with 2 M HCl. By addition of NH_4PF_6, the dipositive ion was precipitated as the yellow salt $[(NH_3)_5Ru(1,2\text{-dithiane})](PF_6)_2$ (I) in 30% overall yield. Anal. Calcd for $C_4H_{23}N_5S_2RuP_2F_{12}$: C, 8.05; H, 3.87; N, 11.74; S, 10.75; Ru, 16.95; F, 38.22. Found: C, 8.06, H, 3.89;

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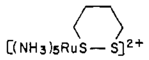
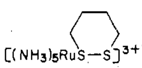
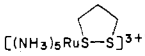
Table I. Visible and UV Spectra of Some Pentaammineruthenium(II) and -(III) Dithiols and Disulfides

complex	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	conditions
$[(NH_3)_5RuSC_2H_5]^{2+}$ [3]	508	1.9×10^3	
$[(NH_3)_5RuS(CH_2)_4SH]^{2+}$ [a]	510	1.2×10^3	0.36 M H_2SO_4; O_2 as oxidant
$[(NH_3)_5RuS(CH_2)_3SH]^{2+}$ [a]	507	6.7×10^2	
$[(NH_3)_5RuSC_6H_5]^{2+}$	485 sh, 500		0.1 M HCl
$[(NH_3)_5RuSeC_6H_5]^{2+}$	590 (composite band)		0.1 M HCl
$[(NH_3)_5RuS(CH_3)_2]^{3+}$	453	300	
	285	930	acidic soln
	220	5×10^3	
$[(NH_3)_5RuS(CH_3)_2]^{2+}$ [3]	358	64	
	258	2.14×10^3	
	235	2.05×10^3	
	325	2.28×10^3	
	225 sh	$\sim 2.1 \times 10^3$	0.1 M HCl;[b] solid prepn
	210	$\sim 5.5 \times 10^3$	
	360 sh	1.1×10^2	
	618	1.71×10^2	
	768	75	

[a] Stage B. [b] For product C (oxidation preparation) the wavelengths recorded were 325, 225 (sh), and 210 (sh) nm. [c] Stage D.

N, 11.72; S, 11.22; Ru, 17.3; F, 38.4.

Preparation of Disulfides by Oxidative Cyclization of Coordinated Dithiols. The procedure starting with 1,4-butanedithiol described below also works well for 1,3-propanedithiol. With 1,6-hexanedithiol, the major product is the 2:1 complex. Although a mononuclear Ru(II) complex is formed by using 1,2-ethanedithiol, oxidation of the species does not cause cyclization but instead produces a polymeric material.

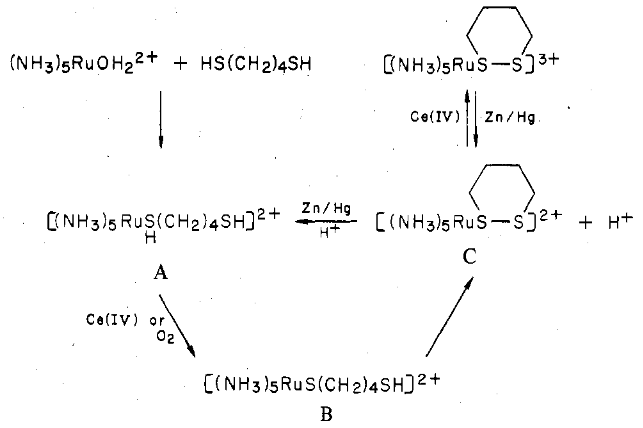
Product A. To prepare the 1:1 complex of Ru(II) with 1,4-butanedithiol, 100 mg of finely powdered $[(NH_3)_5RuCl]Cl_2$ was dissolved in 8 mL of 0.36 M H_2SO_4 and reduced over Zn/Hg. The neat ligand (0.50 mL) was added, whereupon the reaction mixture rapidly became orange. The orange color results from residual oxygen introduced with the ligand; the Ru(III) complex contributing the color is eventually reduced when $[Ru(NH_3)_5OH_2]^{2+}$ is consumed, and thus it provides a convenient way of determining when the reaction is complete. After 1 h, the solution now pale yellow, was extracted three times with chloroform to remove excess ligand. After extraction, the mixture was decanted from the Zn/Hg amalgam and added to an equal volume of 3 M HCl or 3 M H_2SO_4.

Product B. Product A is air sensitive. Oxidation by air or by 1 equiv of Ce(IV) produces a species, B, which from its behavior on a cation-exchange resin is judged to carry a charge of 2+. The species, which is deep red, was eluted from Dowex 50W-X2 ion-exchange resin by 2 M HCl, and the ion-exchanged product was used for the operation described in the next section. Note that in the oxidation with Ce(IV) in 1:1 ratio, Ce(IV) is fully consumed and that a single ruthenium containing product, B, is obtained.

Reaction of product A with air when bubbled through rapidly is complete in ca. 1 min. At this stage, there is a definite arrest in the reaction with O_2, but if contact with O_2 continues, product B does deteriorate slowly, behavior which is noted also for other thiolate complexes of Ru(III).

Product C. When solid $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$ is added stepwise to product B, the color fades, and the fading is complete when the molar ratio of Ce(IV)/product B reaches approximately 1:1. Ion exchange of the product solution shows that only one ruthenium-containing species is present in significant amounts. The major product is yellow and readily elutes in 2 M HCl. A small quantity of a brown material that has not been identified remains on the column even on elution with 6 M HCl.

Scheme I



For good yields, the oxidizing agent must be added in small increments, with vigorous stirring, making certain that the color stabilizes before the next increment is added. Often, the end point is obscured by the appearance of a brown color which masks the pale yellow of the desired product. Side reactions, apparently leading to further oxidation of the ligand, can occur at this stage, but solution yields of product C of >80% can be obtained. The oxidation was done in acidic solution, [HCl] ranging from 0.40 to 2 M, and in 0.36 M H_2SO_4.

The absorption spectrum of product C, as purified by cationic exchange, was taken. The absorption maxima corresponded to those of the complex formed by the direct substitution (cf. Table I), and the ratios of the values of the extinction coefficient at wavelengths of 325 and 225 (sh) nm were the same: ~1.1 for the material prepared by substitution and ~1.0 for that resulting from cyclization by oxidation.

Product D. Further oxidation using Ce(IV) consumes 1 mol of Ce(IV) per mole of product C and produces a blue species; increasing the ratio Ce(IV)/Ru causes no change in the amount of product D formed. This reaction stage is the same whether product C or the material obtained by direct substitution is used. The stage C to D is reversible on the time scale of cyclic voltammetry (vide infra).

On reduction of D, C, or B with Zn/Hg, species A is eventually formed, the progression of color starting with D being blue → green → orange → yellow. On carrying a reaction mixture through the cycle B → C → D → A → B,

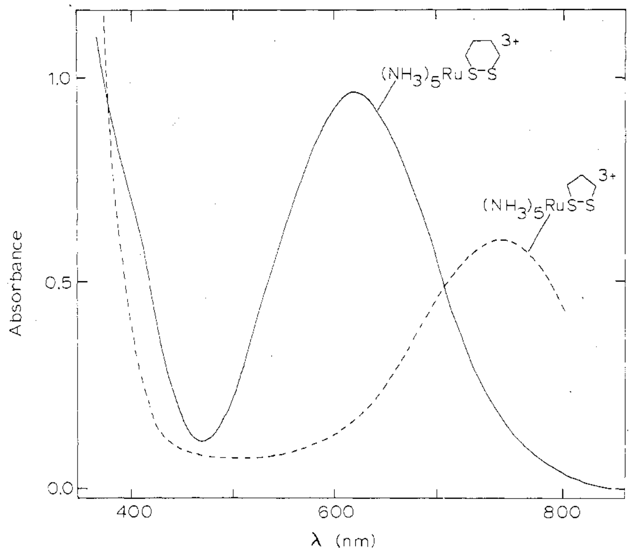


Figure 1. Absorption spectra of disulfide complexes of pentaammineruthenium(III) in 0.1 M HCl (25 °C, 1-cm quartz cells, [Ru] = 5.55 × 10^{-3} M for the six-membered ring; [Ru] = 8.00 × 10^{-3} for the five-membered ring).

we observed that ca. 80% of B was restored, as judged by the absorption in the visible characteristic of B. Significant loss, as already acknowledged, can occur in taking product B to C.

An outline of the chemistry involving products A to D is given in Scheme I. For clarity, but anticipating the discussion to follow, the formulas for the species are also included.

The reactions using 1,3-propanedithiol as ligand follow the same course as those described for 1,4-butanethiol, but in this case, on repetition of the cycle analogous to that described for the latter, only 72% of the stage B species was restored. The principal loss, as before, occurs in the B → C step. Loss of ligand from ruthenium in stage D does occur; for the complex derived from 1,3-propanedithiol, the half-life for the aquation reaction in 1.5 M HCl at 25 °C was found to be 100 min.

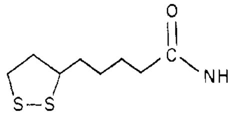
A remarkable feature of the oxidation from stage B to C is that the nature of the product is dependent on the oxidizing agent. Oxidation takes place also when $FeCl_3$(aq) or *cis*-$[(NH_3)_4Ru(\text{benzonitrile})_2]^{3+}$ (E_f = 890 nm vs. NHE; prepared from the 2+ complex by using Ce(IV) as oxidant) acts on the stage B complex derived from 1,3-propanedithiol. The reactions were performed in 0.2 M HCl at 25 °C; in neither case was a significant amount of a pentaammine complex of charge 2+ detected, but rather one of much higher charge, ca. 4+.

Characterization. The oxidation of product C is reversible in cyclic voltammetry, at least at the sweep rates used, 100 or 200 mV s^{-1}; E_f for the one-electron couple D/C was measured as 630 mV vs. NHE at 25 °C. No reducing wave corresponding to C → B was observed down to potentials as low as −100 mV. However, when $[(NH_3)_5RuOH_2]^{2+}$ is added to C, an orange solution is produced, which from its appearance is believed to contain at least some of form B.

In Table I are summarized data on the absorption spectra of species derived from 1,4-butanedithiol and 1,3-propanedithiol and included as well are observations on related species. Figure 1 shows the absorption spectra for the two stage D species. Band maxima and corresponding values of ϵ are entered in Table I.

Miscellaneous Experiments. The first attempts to prepare dichalcogenide complexes of Ru(II) were made with diphenyl disulfide and diphenyl diselenide. However, the only products even when a large excess of ligand over $[(NH_3)_5RuOH_2]^{2+}$ was used were the products of the simple redox reaction, namely, $[(NH_3)_5RuSC_6H_5]^{2+}$ and $[(NH_3)_5RuSeC_6H_5]^{2+}$. The reaction of $[(NH_3)_5RuOH_2]^{2+}$ with PhTeTePh is complex, and unexplained color changes take place during the reaction.

The first attempts with a cyclic disulfide were made with lipoamide:



Reaction of stoichiometric amounts of this ligand with $A_5RuOH_2^{2+}$ in 1:1 acetone/methanol quickly produced a brown solution. A CV taken of the crude mixture after addition of $[(n\text{-}C_4H_9)_4N](PF_6)$ revealed a reversible wave at +650 mV vs. SCE. The crude mixture was transferred onto an ion-exchange resin (Dowex 50W-X2), but the bulk of the product could not be removed from the column even in 6 M HCl. The results were similar with either excess ligand (fivefold) or excess $[(NH_3)_5RuOH_2]^{2+}$ (fourfold), although in the latter case a small amount of an orange material was eluted by 4 M HCl.

The behavior described suggested that polymerization of the disulfide ligand is occurring, which, according to Wang's observations[6] on the reaction of ferrocene with lipoic acid, can reasonably be construed as resulting from the one-electron reduction of the disulfide by $[(NH_3)_5RuOH_2]^{2+}$. It seemed that it would then be advantageous to use a Ru(II) complex which is more weakly reducing, and, accordingly, the preparation was attempted by using *trans*-$[\text{isn}(NH_3)_4RuOH_2]^{2+}$.

A mixture was prepared containing 100 mg of *trans*-$[\text{isn}(NH_3)_4RuOH_2](PF_6)_2$ and 200 mg of lipoamide in 5 mL of acetone and left to react for 1 h. The mixture was filtered and the solution evaporated to dryness. A reversible wave at E_f = +830 mV vs. NHE (0.1 M HCl) was observed in the product solution, and the complex appeared to be a dication as determined by ion-exchange chromatography. (Only one product was observed on the column.) However, attempted precipitation with a variety of anions (PF_6^-, ClO_4^-, $S_2O_6^{2-}$, BPh_4^-, Reineckate$^-$) gave either no solid or an extremely impure material. Nevertheless, the results were encouraging and led to the surmise that a ligand which did not undergo polymerization with such facility as lipoamide would form a stable adduct with ruthenium ammines, whereupon we chose 1,2-dithiane as ligand.

Discussion

The reaction of 1,2-dithiane with $[(NH_3)_5RuOH_2]^{2+}$ is reasonably straightforward, and in view of the analysis of the solid product which is obtained, there seems to be no question but that it is the desired product. Confirmatory evidence is provided by the observation that the two-electron oxidation of the species formed by the substitution of 1,4-butanedithiol on $[(NH_3)_5RuOH_2]^{2+}$ is identical with that produced from the cation and 1,2-dithiane. On the basis of the method of preparation, which has proven to be successful with other thiol and dithiol ligands, and from the behavior of the species itself, product A is taken to be $[(NH_3)_5RuS(H)(CH_2)_4SH]^{2+}$. This assignment is confirmed by the properties of the one-electron oxidation product B, which has absorption characteristics expected for $[(NH_3)_5RuS(CH_2)_4SH]^{2+}$—here note the similarity of the absorption spectra for the two B-stage products to that of $[(NH_3)_5RuSC_2H_5]^{2+}$. The reaction taking product B to product C then can be represented as

$$[(NH_3)_5RuS(CH_2)_4SH]^{2+} + Ce(IV) \rightarrow [(NH_3)_5Ru(1,2\text{-dithiane})]^{2+} + Ce(III) + H^+$$

A reaction such as this involving extensive bond rearrangement is expected to be slow on the cyclic voltammetry time scale, as is the case for the product B to C transformation. The final stage then, C to D, now reversible on the cyclic voltammetry time scale, is the simple electron extraction

$$[(NH_3)_5Ru(1,2\text{-dithiane})]^{2+} \rightarrow [(NH_3)_5Ru(1,2\text{-dithiane})]^{3+} + e^-$$

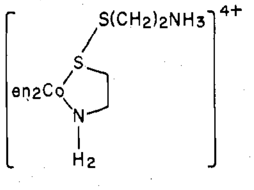
To our knowledge, the formation of a coordinated cyclic disulfide by oxidation has not previously been described, although oxidative coupling to produce an unstable binuclear disulfide has been reported.[7] A remarkable feature of the cyclization step is the way the yield of cyclized product depends on the nature of the oxidizing agent. Cerium(IV), but not Fe^{3+}(aq) or a ruthenium(III) bis(nitrile) complex, leads to a cyclized product. If cyclization involves a Ru(IV) complex as an intermediate, the difference can be understood.

$$[(NH_3)_5Ru^{IV}S(CH_2)_4SH]^{3+} \rightarrow [(NH_3)_5Ru(1,2\text{-dithiane})]^{2+} + H^+$$

It is reasonable to suppose that of the three oxidants only Ce(IV) is strong enough to generate Ru(IV). The other oxidants have available only the alternative of converting the exo thiol function to a radical, which then can dimerize to produce a molecule of high charge. It will be noted that implicit in this interpretation is the assumption that Ce(IV) more rapidly oxidizes Ru(III) than it does the exo thiol, an assumption which at our present state of knowledge is ad hoc.

Turning now to a second major point, the absorption spectra of the Ru(III) disulfide complexes, we note from Figure 1 and Table I that absorption is observed at energies much lower than is characteristic of a simple sulfur-containing ligand, whether that is a thioether or a thiol. We attribute the absorption at 618 nm for the six-membered ring and that at 768 for the five-membered ring to charge transfer from the antibonding (n^-) level arising from the sulfur lone-pair interaction on the disulfide group. The shoulder at 360 nm observed for the complex of the six-membered ring is likely the complementary transition from the bonding component. The splitting of these bonding and antibonding states then for the six-membered ring when bound to Ru(III) is ca. 1.4 eV to be compared to 0.95 for the free ligand.[11] For the five-membered ring, the shift to lower energies is more pronounced than for the six, and the splitting is apparently so great that the higher energy component is buried in other absorption at shorter wavelengths. The splitting in the complex on this basis exceeds 1.8 eV. A value has not been found in the literature for the free ligand, but for lipoic acid which has the same ring structure, 1.8 eV has been reported as the splitting arising from sulfur lone-pair interactions.[8] The splittings for the complexes are not expected to be the same as they are for the free ligands because in the 1:1 complexes the degeneracy of the sulfur lone pairs is already lifted by attaching a metal to one of the atoms. In some but not all cases, the splittings are larger for the 1:1 complexes than those for the free ligands.[1,9] In any event, the observation made for the complexed ligands also supports the idea[10,11] that the lone-pair splitting depends on the lone-pair dihedral angle, this being smaller for the five- than for the six-membered ring.

Sulfur lone-pair perturbations can explain why in the near-UV two bands of rather high intensity ($>10^3$ M^{-1} cm^{-1}) are observed in the absorption spectrum of



but only one when the $S(CH_2)_2NH_3$ side chain is missing.[7]

The effects have here been called "lone-pair perturbations" because they are also encountered when atoms are not directly bonded, but they are, of course, implicit in the molecular orbital description of a disulfide or peroxide unit as splitting of π and π^* levels. They are responsible for the fact that Ti^{IV}–OOH, for example, shows light absorption at much lower energy than does Ti–OH. Titanium(IV) coordinated to OH^- is colorless, but the titanium(IV) peroxide complex even in acid solution is orange to red. For Ti(IV) in 96% H_2SO_4, a band maximum is reported[12] at 430 nm, ϵ 127 M^{-1} cm^{-1}. There is rising absorption at shorter wavelengths, very much higher than can be ascribed to H_2O_2, and apparently a second band is present, which cannot so definitively be assigned (it may be $\pi d \leftarrow p\sigma^*$). Much the same features are observed for V^V–OOH, except that the low-energy band appears at still longer wavelengths; less strongly oxidizing metal centers from complexes which are much less highly colored and have the absorption shifted to short wavelengths.

We further suggest that the long-wavelength absorption reported for $[(NH_3)_5RuS)_2]^{4+}$,[13] and which has hitherto not been explained, has a similar origin. The lone pairs on the bridging disulfur unit interact, and thus the transition at 720 nm (ϵ 1.7×10^4 M^{-1} cm^{-1}) can be assigned to $\pi d \rightarrow n^-$ transition with the $\pi d \rightarrow n^+$ then being promoted to much higher energies. This interpretation does not of itself explain the effect on the long-wavelength transition of replacing NH_3 trans to the bridging group by other ligands, but it does at least suggest that no simple relation between the properties of the ligands and the band energies is to be expected. In altering the energy of the acceptor orbital on Ru(III) (i.e., the potential of the 3+/2+ couple), the ligands will affect the energy gap between this orbital and the center of gravity of the n^+–n^- lone-pair combination, but the ligands can also be expected to affect the splitting itself, electron-releasing ligands such as I^- increasing the splitting.

Evidence of perturbations arising from lone-pair interactions can be discerned also in the charge-transfer spectra of complexes of $C_6H_5S^-$ and $C_6H_5Se^-$ with Ru(III) (cf. Table I). The bands in the visible region in both cases are composite. The splitting, in this case much less than for the disulfide complexes, presumably arises from the interaction of the lone pairs on the chalcogen atom with the π cloud of the aromatic ring.

Finally, attention is directed to the absorption spectrum of the Ru(II) complex of 1,2-dithiane. The two bands at longer wavelength presumably have the same origin as the two recorded for the dimethyl sulfide complex and correspond to transitions from a πd level on Ru(II) to some level on sulfur. In an earlier paper,[3] the acceptor level on sulfur was taken to be 3d, but there is no assurance whatever that it was correctly assigned. Elsewhere[9] the suggestion is made that the acceptor orbitals are in fact σ^*. This interpretation has an immediate advantage in the present context. The σ^* level arising from a S–S interaction is expected to lie lower than that from C–S, and this provides a simple explanation of the fact that the long-wavelength transition lies considerably lower for the 1,2-dithiane as ligand than for dimethyl sulfide. Ligand absorption is weak[5] in the spectral region under discussion (295 nm, 3×10^2 M^{-1} cm^{-1}; 240 nm sh, ϵ 2×10^2 M^{-1} cm^{-1}) but probably accounts for the sharp rise noted just short of 210 nm for the 1,2-dithiane complex.

It has been assumed throughout that in the disulfide complex Ru is bound to only one sulfur. A referee has suggested that the metal might be symmetrically bound to two. Such a structure has not been ruled out by direct observations, but in view of the electronic structure of Ru(II), low-spin d^6, it seems to us to be very unlikely.

Acknowledgment. Support of this research by NIH Grant No. GM13638 (Biochemically Significant Molecules as Ligands) is gratefully acknowledged.

Registry No. $[(NH_3)_5Ru(1,2\text{-dithiane})](PF_6)_2$, 70288-18-5; $[(NH_3)_5Ru(1,2\text{-dithiane})]^{3+}$, 70288-19-6; $[(NH_3)_5Ru(1,2\text{-dithiol-$

ane)]$^{3+}$, 70304-28-8; [$(NH_3)_5RuS(CH_2)_4SH$]$^{2+}$, 70288-20-9; [$(NH_3)_5RuS(CH_2)_3SH$]$^{2+}$, 70288-21-0; [$(NH_3)_5RuSC_6H_5$]$(PF_6)_2$, 70288-23-2; [$(NH_3)_5RuSeC_6H_5$]$(PF_6)_2$, 70288-25-4; [$(NH_3)_5RuS(CH_3)_2$]$^{3+}$, 69204-65-5; [$(NH_3)_5RuS(H)(CH_2)_4SH$]$^{2+}$, 70288-26-5; [$(NH_3)_5RuOH_2$]$(PF_6)_2$, 34843-18-0; [$(NH_3)_5RuCl$]Cl_2, 18532-87-1; diphenyl disulfide, 882-33-7; diphenyl diselenide, 1666-13-3.

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Crystal Structures of *cis*-Tetraamminebis(isonicotinamide)ruthenium(II) and -(III) Perchlorates

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Single crystals of *cis*-[$Ru(NH_3)_4(isn)_2$]$(ClO_4)_3\cdot H_2O$ (I) and *cis*-[$Ru(NH_3)_4(isn)_2$]$(ClO_4)_2$ (II) (isn = isonicotinamide) have been studied by X-ray structural analysis. Both I and II crystallize in the centrosymmetric monoclinic space group $P2_1/n$. For I, $a = 15.337$ (15) Å, $b = 10.636$ (8) Å, $c = 17.467$ (16) Å, $\beta = 110.78$ (7)°, $V = 2264$ (4) Å^3, and ρ(calcd) = 1.82 g cm^{-3} for $Z = 4$ and mol wt 729.82. For II, $a = 12.206$ (4) Å, $b = 23.986$ (15) Å, $c = 7.749$ (2) Å, $\beta = 93.88$ (3)°, $V = 2264$ (2) Å^3, and ρ(calcd) = 1.80 g cm^{-3} for $Z = 4$ and mol wt 612.35. Diffraction data for $0.6° < 2\theta < 45°$ (Mo K$\bar{\alpha}$ radiation) were collected on a Syntex $P2_1$ automated diffractometer. The structures were solved by the usual Patterson, Fourier, and least-squares refinement techniques. In both solutions, all atoms other than hydrogen were located directly. The structure of I was refined to $R_F = 4.7\%$ and $R_{wF} = 6.5\%$ for the 3080 reflections with $F_o^2 > 3\sigma(F_o)^2$. The structure of II was refined to $R_F = 4.8\%$ and $R_{wF} = 6.4\%$ for 2246 reflections. The weighted means for Ru^{III}–NH_3 and axial Ru^{II}–NH_3 bond distances are 2.125 (7) and 2.143 (5) Å, respectively. The Ru–NH_3 bond distances for the ammonias trans to isonicotinamides in II are consistently longer (weighted mean 2.170 (6) Å) than the axial distances, and a statistical analysis indicates that a small trans influence is present for II. The weighted means for Ru^{III}–N(isn) and Ru^{II}–N(isn) bond lengths are 2.099 (4) and 2.060 (4) Å. The decrease in Ru–N(isn) bond length for the Ru(II) state is attributed to dπ–π^* interactions.

Introduction

Crystallographic metal–ligand distances have been used to estimate the contribution of the inner-sphere reorganization energy to the activation energy of electron-transfer reactions.[1] Such calculations also require a knowledge of the force constants for the relevant metal–ligand bonds.[1-3] As the difference in metal–ligand distances for the two oxidation states involved in a self-exchange process decreases, the free energy of activation due to inner-sphere reorganization (ΔG_i^*) becomes smaller if the force constants are assumed to be unchanged. Thus, the increased rate of self-exchange for [$Fe(phen)_3$]$^{2+/3+}$[4] over [$Fe(H_2O)_6$]$^{2+/3+}$ is thought to be due in part to the small difference between the Fe^{II}–N and Fe^{III}–N distances in the former case.[1] The remainder of the difference in rates is accounted for by the solvent (ΔG_o^*) and electrostatic work (w_e) contributions to the overall activation energy for self-exchange if the reactions are adiabatic.

Ruthenium provides especially attractive self-exchange systems for testing theoretical expressions of the above type. In many cases, reduction of a ruthenium(III) complex to the ruthenium(II) state does not introduce excessive liability to the ion, thus making possible accurate determinations of self-exchange rates for many closely related systems. Such a series is that in which the ammonias of [$Ru(NH_3)_6$]$^{n+}$ (n = 2, 3) are successively replaced with π acids.

Stynes and Ibers[5] have determined the molecular structures of [$Ru(NH_3)_6$]I_2 and [$Ru(NH_3)_6$]$(BF_4)_3$ and conclude that the inner-sphere distortion necessary to form the activated complex can be attained easily at room temperature. Brown and Sutin[6] have suggested that ΔG_i^* is small in comparison to the ΔG_o^* term for ruthenium(II) and -(III) self-exchange. They propose that the large increase in self-exchange rate on going from [$Ru(NH_3)_6$]$^{2+/3+}$ to [$Ru(bpy)_3$]$^{2+/3+}$ (a factor of approximately 10^5) is primarily due to the change in the radii of the cations rather than to a decrease in ΔG_i^*.

If the term ΔG_i^* is to be accurately estimated from theoretical expressions for the series [$Ru(NH_3)_6$]$^{2+/3+}$, [$Ru(NH_3)_5L$]$^{2+/3+}$, [$Ru(NH_3)_4L_2$]$^{2+/3+}$, ..., [RuL_6]$^{2+/3+}$ (L = π acceptor such as py, isn, or pyz), then accurate molecular dimensions must be known. Preliminary results of Wells and Creutz[7] for the complexes [$Ru(NH_3)_5pyz$]$(BF_4)_2$ and [$Ru(NH_3)_5pyz$]$(CF_3SO_3)_3$ indicate that there is a substantially shorter Ru–N(pyz) distance in the ruthenium(II) complex. We have determined the crystal structures of *cis*-[$Ru(NH_3)_4(isn)_2$]$(ClO_4)_2$ and *cis*-[$Ru(NH_3)_4(isn)_2$]$(ClO_4)_3\cdot H_2O$ to observe the effect of two π acceptors on the molecular dimensions.

Crystal structures have also proven useful in demonstrating the presence of back-bonding in ruthenium(II) complexes with π-acceptor ligands. In such cases the metal-ligand bond length is significantly less for the π-acceptor ligand than for a ligand with the same donor atom but no π-acceptor capability. The effect has been clearly observed in [$Ru(NH_3)_5NO_2$]Cl,[8] [$Ru(NH_3)_5NO$]Cl_2,[9] [$Ru(OH)(NH_3)_4NO$]Cl_2,[9] [$(Ru(NH_3)_5)_2N_2$]$(BF_4)_2$,[10] and [$(Ru(py)_4)_2C_2O_4$]$(BF_4)_2$,[11] where NO_2^-, NO^+, N_2, and pyridine are believed to participate in dπ–π^* bonding interactions. In some of the above compounds, a trans influence is observed;[8,10] that is, the ligands coaxial

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