

Binuclear Ruthenium Complexes Bridged by the Dicyanamide Anion

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As shown by the value of the extinction coefficient for the intervalence band for μ -dicyanamido-bis(pentaammineruthenium)(4+), ϵ 2.8×10^3 M⁻¹ cm⁻¹, dicyanamide ion as a bridging group produces quite strong electronic coupling in the mixed-valence molecule. A number of properties, among them the bandwidth at half-height, the dependence of the band energy on solvent properties, and the rather small value of the comproportionation constant, 3.4×10^2 , show the species to be valence trapped. Replacing trans ammonias by pyridine or by isonicotinamide decreases the electronic coupling, suggesting that the dominant coupling mechanism, in spite of the negative charge on the ligand, is $\pi d-\pi^*$ delocalization rather than $\pi d-\pi$.

The most intense intervalence absorption thus far reported for a mixed-valence molecule based on the Ru(III)-Ru(II) couple is that for the anion derived from *tert*-butylmalononitrile, where the value of ϵ at the maximum, $\lambda = 1170$ nm, is 1.6×10^4 M⁻¹ cm⁻¹.^{1,2} For this system, the principal coupling mechanism almost certainly involves the electron pair freed by the release of the proton from the bridging ligand; i.e., it depends on mixing the state Ru^{II}[neutral radical]Ru^{II} with the ground state. A serious limitation in the study of the μ -[malononitrile(1-)] species is their instability, but this is much less a problem with the related species with dicyanamide (N(CN)₂⁻) as the bridging group. The research to be described was devoted to the characterization of mononuclear and binuclear ruthenium complexes of this bridging group, a special effort having been made to ascertain whether the principal mechanism for interaction in the mixed-valence states is the same as for the μ -[malononitrile(1-)] species. The alternative mechanism involves admixture into the ground state of states based on Ru^{III}[radical dianion]Ru^{III}. This mechanism is likely the dominant one in the molecule³ [(NH₃)₅RuNCCNRu(NH₃)₅]⁵⁺. When π (ligand)- πd delocalization is the dominant coupling mechanism, it is expected that if a molecule of NH₃ on each metal is replaced by an electron-withdrawing ligand, thereby increasing the reduction potential of the Ru(III)/Ru(II) couple, the interaction between the metal centers will be enhanced. At any rate, the strategy which was used in trying to determine the dominant coupling mechanism in the μ -dicyanamide species is based on this idea.

Experimental Section

Materials. Sodium dicyanamide was purchased from Aldrich and was used without further purification. Isonicotinamide was obtained from Eastman and purified by repeated crystallization. Europium oxide purchased from Research Chemicals was used to prepare europium(II) in acidic media by reduction over zinc amalgam.

Argon and chlorine gases were purchased from Liquid Carbonic. The argon (99.995%) was freed of oxygen by passing it through a scrubbing tower charged with 0.25 M chromium(II) (from Cr(ClO₄)₃) in 0.5 M perchloric acid over Zn amalgam and dried by passage through a second tower containing sulfuric acid. The chlorine was used as supplied.

House-line distilled water was purified by redistillation from alkaline permanganate in an all glass still.

Deuterium chloride (12.1 M in D₂O) was purchased from International Chemical and Nuclear and diluted with D₂O (MSD Isotopes, Merck) to the desired concentrations.

The chromatographic separations were made with Sephadex-SP-C25-120 strongly acidic cation-exchange resin purchased from Sigma. The resin was allowed to swell in water before packing the column with the resin slurry. The column was cleaned by elution with 2 M HCl and then with distilled water.

Ruthenium Complexes. Hexaammineruthenium chloride was purchased from Matthey Bishop, Inc., and converted into the corre-

sponding chloropentaammineruthenium(III) chloride following literature procedures.⁴

Caution! Perchlorate salts of ruthenium complexes should be prepared only in small amounts and handled cautiously. Although no shock-induced explosions were encountered in the course of our work, we found that heating resulted in detonation.

Pentaammineaquoruthenium(III) trifluoromethanesulfonate was the source of the pentaammineruthenium moiety. It was prepared from [Ru(NH₃)₅OH]S₂O₆⁵⁻ by dissolving the latter in 3 M trifluoromethanesulfonic acid, exercising care to keep the pH below 1, and filtering, whereupon an equal volume of 8 M trifluoromethanesulfonic acid was added to the filtrate, and the resulting solution was stored in the refrigerator. The precipitate, off white, was collected, washed with ether, and air-dried; yield greater than 90%.

trans-Tetraamminechloro(sulfur dioxide)ruthenium(II) chloride was prepared according to Isied's procedure.⁶

trans-Tetraammine(pyridine)(sulfato)ruthenium(III) chloride was prepared according to the procedure outlined by Isied⁶ and purified as indicated.

trans-[Ru(NH₃)₄SO₂Cl]Cl (100 mg) was added to 3 mL of argon-purged water. Sodium carbonate was added to adjust the pH to about 9. A few drops of pyridine was added and the reaction allowed to continue for 5 min. To the resulting light yellow-orange solution was added 2 mL of 6 M HCl, producing a brown solution which was promptly oxidized by adding 2 mL of 30% H₂O₂. The resulting pale yellow solution was added to 100 mL of rapidly stirred acetone. The precipitate which formed was filtered, washed with acetone and ether, and air-dried. The crude product was dissolved in distilled water and was purified by ion-exchange chromatography using the resin described above. After it was loaded, the column was first eluted with distilled water to remove excess ligand. Elution was continued with 0.05 M HCl until the first yellow band traveled the length of the column, at which time 0.1 M HCl was used to complete elution of this band. The eluent was rotary evaporated to dryness and the residue dissolved in a small amount of 6 M HCl. The solution was filtered to remove sodium chloride, and the product was precipitated by adding the filtrate to acetone as before. The product was recrystallized by dissolving the residue in 1 mL of 1 M HCl, adding about 5-10 mL of ethanol, and cooling in the freezer. The product was collected and then washed with ethanol and ether before drying; yield 75 mg (60%). Anal. Calcd for [Ru(NH₃)₄(SO₄)py]Cl: C, 15.81; H, 4.51; N, 18.47. Found: C, 15.73; H, 4.54; N, 18.47.

Dicyanamidopentaammineruthenium(II) hexafluorophosphate was prepared as follows. A solution of 0.25 g [Ru(NH₃)₅H₂O](CF₃SO₃)₃ in 10 mL of 0.01 M HCF₃SO₃ was warmed to 50-60 °C on a water bath while a stream of argon passed through the solution. A 10-20-fold excess of sodium dicyanamide was added, and the mixture was left for 3 h. It was then cooled to room temperature and 1-2 mL of saturated NH₄PF₆ was added. A red-orange precipitate formed. It was collected and washed with ethanol and ether and then vacuum-dried. Anal. Calcd for [Ru(NH₃)₅(N(CN)₂)](PF₆)₂: C, 4.43; H, 2.79; N, 20.67. Found: C, 4.60; H, 2.87; N, 20.61. Yield, > 70%.

μ -Dicyanamide-bis(pentaammineruthenium(II)) Hexafluorophosphate. A solution of [Ru(NH₃)₅H₂O](CF₃SO₃)₃ was prepared

(1) Krentzien, H.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 6371.

(2) Krentzien, H. Ph.D. Thesis, Stanford University, 1976.

(3) Tom, Glenn M.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 5310.(4) Vogt, L.; Katz, J.; Wiberley, S. *Inorg. Chem.* **1965**, *4*, 1157.(5) Gleu, K.; Breuel, K. *Z. Anorg. Allg. Chem.* **1938**, *237*, 335. Gleu, K.; Buddecker, I. *Ibid.* **1952**, *268*, 202.

(6) Isied, S. S. Ph.D. Thesis, Stanford University, 1974.

by dissolving 0.8 mmol in 10 mL of 0.01 M HCF_3SO_3 , and 0.4 mmol of $\text{NaN}(\text{CN})_2$ was added. The reaction solution was degassed for 10 min and then reduced for 3 h under continuous argon flow with zinc amalgam. The resulting solution was filtered under N_2 in a glovebag, and 2 mL of a degassed saturated solution of NH_4PF_6 in 0.1 M $\text{CF}_3\text{SO}_3\text{H}$ was added. The precipitate was collected, washed with deaerated ethanol and then ether, and vacuum-dried. It should be noted that the complex is protonated in the solid. Anal. Calcd for $[(\text{Ru}(\text{NH}_3)_5)_2\text{HN}(\text{CN})_2](\text{PF}_6)_4$: C, 2.36; H, 3.06; N, 17.86; Ru, 19.83. Found: C, 2.20; H, 3.16; N, 18.08; Ru, 19.90.

***trans*-Tetraammine(isonicotinamide)(sulfato)ruthenium(II) chloride.**

The procedure as outlined for the pyridine analogue was used to prepare this complex; yield 90 mg (65%). Anal. Calcd for $[\text{Ru}(\text{NH}_3)(\text{SO}_4)\text{isn}]\text{Cl}$: C, 17.08; H, 4.30; N, 19.93. Found: C, 17.29; H, 4.35; N, 20.03.

μ -Dicyanamido-bis(*trans*-(pyridine)tetraammineruthenium(III))

Perchlorate. *trans*- $[\text{Ru}(\text{NH}_3)_4\text{SO}_4\text{py}]\text{Cl}$ (75 mg) and 0.5 equiv of sodium dicyanamide were dissolved in 2 mL of water and the solution degassed with argon and then reduced with zinc amalgam for 4 h. The reaction mixture was filtered and oxidized with chlorine gas. A solid was precipitated by adding the solution to 150 mL of rapidly stirred acetone and collected. The crude product was dissolved in 10 mL of water and precipitated by adding 1 mL of saturated aqueous sodium dithionite. The crystalline dithionite salt was collected and added to 10 mL of rapidly stirred, saturated aqueous sodium perchlorate. After 30 min of stirring, the perchlorate salt was collected, dissolved in 2 mL of water, and recrystallized by adding a few drops of saturated aqueous sodium perchlorate. The final product was collected, washed with ethanol and ether, and dried in a vacuum desiccator; yield 40 mg (18%). Anal. Calcd for $[(\text{Ru}(\text{NH}_3)_4\text{py})_2(\text{N}(\text{CN})_2)(\text{ClO}_4)_5]$: C, 13.59; H, 3.23; N, 17.18. Found: C, 13.88; H, 3.28; N, 17.03.

μ -Dicyanamido-bis(*trans*-(isonicotinamide)tetraammineruthenium(III)) Perchlorate Trihydrate. This compound was prepared by a procedure analogous to that used for the corresponding pyridine complex except for the purification step.

The crude product was dissolved in a minimum amount of water and reprecipitated as a perchlorate salt by adding solid sodium perchlorate. This material was collected and recrystallized by dissolving it in 2.5 mL of water and adding an equal volume of 0.2 M sodium perchlorate. The crystals produced after cooling in an ice bath were collected, washed with ethanol and ether, and dried in a vacuum desiccator, yield 22%. Anal. Calcd for $[(\text{Ru}(\text{NH}_3)_4\text{isn})_2\text{N}(\text{CN})_2](\text{ClO}_4)_5 \cdot 3\text{H}_2\text{O}$ (isn = isonicotinamide): C, 14.02; H, 3.53; N, 17.52; Cl, 14.78. Found: C, 13.72; H, 3.35; N, 17.35; Cl, 14.48.

Instrumentation. Electronic spectra were recorded in the UV, visible, and near-IR regions with matched quartz cells, on a Beckman Model 5270 spectrophotometer.

Electrochemistry. Electrochemical measurements were made with a Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer system. Formal reduction potentials ($E_{1/2}$) were measured by cyclic voltammetry using a carbon-paste electrode. Carbon paste was purchased from Bio-Rad, Inc., and packed into the cavity of a Teflon plug fitted with a copper wire to form a lead and held in a glass tube. Potentials were measured against a saturated calomel electrode (SCE Beckman Model 39190) and are uncorrected for junction potentials. Potentials were corrected to the hydrogen scale by adding 0.244 V. The voltammetric measurements were made in a standard H-cell with the test solution compartment separated from the reference electrode compartment by a fine-porosity glass frit. A platinum wire was used as an auxiliary electrode.

Determination of Comproportionation Constants. Comproportionation constants were determined by a spectrophotometric titration of the intervalence-transfer transition characteristic of the mixed-valence oxidation state using the procedure reported in the literature.⁷ The two redox stages for the bis(pentaammine) species are well enough separated so that ΔE could be read directly from the cyclic voltammogram.

Results

UV-Visible Absorption. In Table I the salient features of the absorption spectra of the binuclear complexes in the UV-

Table I. UV-Visible Spectra of Dicyanamide-Bridged Binuclear Complexes^a

| Ru moiety ^b | [2,2] ^c | | [2,3] ^d | | [3,3] | |
|---|--------------------|----------------|--------------------|----------------|----------------|----------------|
| | λ , nm | log ϵ | λ , nm | log ϵ | λ , nm | log ϵ |
| $\text{Ru}(\text{NH}_3)_5$ | 223 | 4.40 | | | 326 | 3.40 |
| | 323 | 3.50 | | | 400 | 3.30 |
| <i>trans</i> - $\text{Ru}(\text{NH}_3)_4\text{py}$ | ~240 | sh | 241 | sh | 259 | 4.17 |
| | 409 | 4.35 | 340 | sh | 320 | sh |
| | | | 400 | 4.11 | 428 | 3.60 |
| <i>trans</i> - $\text{Ru}(\text{NH}_3)_4\text{isn}$ | 219 | 4.56 | 260 | sh | 277 | 4.17 |
| | 260 | sh | 350 | sh | 335 | sh |
| | 350 | sh | 471 | 4.20 | 440 | 3.58 |
| | 486 | 4.44 | | | | |

^a Measured in 0.1 M HCl. ^b py = pyridine; isn = isonicotinamide.

^c Obtained by reducing [3,3] with Zn/Hg amalgam or Eu^{2+} .

^d Obtained by mixing equal concentrations of [2,2] and [3,3].

These spectra have not been corrected for the small amounts of the isoivalent forms present in the solutions.

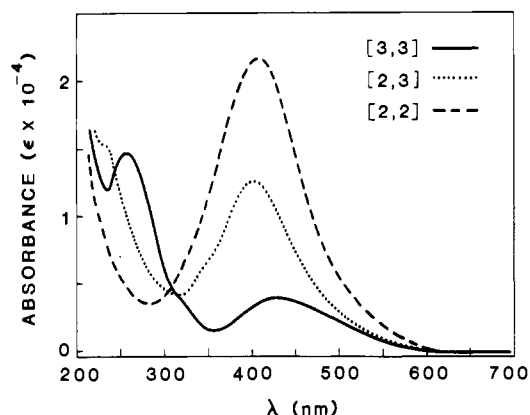


Figure 1. UV-visible spectra of $[(\text{trans-Ru}(\text{NH}_3)_4\text{py})_2\text{N}(\text{CN})_2]^{3+,4+,5+}$, in 0.1 M HCl. [2,3] spectrum not corrected for comproportionation.

visible region are summarized. In Figure 1, the traces for the three oxidation states for one of the systems, namely, that based on the *trans*-pyridine moiety are shown. It is clear that the mixed oxidation state shows all the features of the isoivalent forms, and this is true also of the other two binuclear systems. In view of the fact that a proton is incorporated into the solid when $[(\text{Ru}(\text{NH}_3)_5)_2\text{N}(\text{CN})_2]^{3+}$ precipitates as the hexafluorophosphate salt, the possibility of protonation in solution must be taken into account. The absorption spectrum in the UV-visible region was found to be unaltered over the pH range 0.8–7.

The very intense absorption at 223 nm for $[(\text{Ru}(\text{NH}_3)_5)_2\text{N}(\text{CN})_2]^{3+}$ can be assigned as metal-to-ligand charge transfer; absorption in this wavelength region is registered by other nitriles ($\lambda_{\text{max}} = 229$ nm for $[\text{Ru}(\text{NH}_3)_5\text{CH}_3\text{CN}]^{2+}$).⁸ The origin of the rather intense absorption at 323 nm is not understood. The intensity is too high for it to arise from a d-d transition. The information on the absorption of the mononuclear species is unfortunately incomplete owing to instability of the ion, and only a band at 220 nm can be assigned with confidence to the ion. The major feature of the absorption in the fully reduced state when a *trans* ammonia is substituted by pyridine or isonicotinamide is the metal-to-heterocyclic absorptions at 400 nm and 486 nm, respectively. These correspond to bands at 407 and 497 nm for the pentaammine(heterocyclic)ruthenium(II) species.⁹ Discernible too is the $\pi^* \leftarrow \pi$ transition which appears as a shoulder at ~240 nm (at 244 nm⁹ for $[\text{Ru}(\text{NH}_3)_5\text{py}]^{2+}$). The shoulder

(7) Sutton, J. E.; Sutton, P. M.; Taube, H. *Inorg. Chem.* 1979, 18, 1017. Sutton, J. E.; Taube, H. *Ibid.* 1981, 20, 3125.

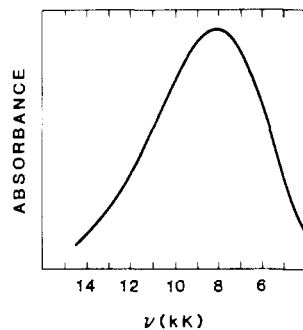
(8) Clarke, R. E.; Ford, P. C. *Inorg. Chem.* 1970, 9, 227.

(9) Ford, P.; Rudd, DeF. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* 1968, 90, 1187.

Table II. Near-Infrared Spectra of Mixed-Valence Dicyanamide-Bridged Binuclear Complexes^a

| Ru moieties ^b | λ_{\max} , nm | $10^{-3}\epsilon$, ^c M ⁻¹ cm ⁻¹ | $10^{-3}\Delta\nu_{1/2}$, cm ⁻¹ | | $10^2 f$ ^e |
|---|-----------------------|--|--|--------------------|-----------------------|
| | | | obsd | calcd ^d | |
| Ru(NH ₃) ₅ | 1100 | 2.82 | 6.20 | 4.58 | 8.04 |
| <i>trans</i> -Ru(NH ₃) ₄ py | 1220 | 2.53 | 6.00 | 4.35 | 6.98 |
| <i>trans</i> -Ru(NH ₃) ₄ isn | 1250 | 2.31 | 5.95 | 4.30 | 6.32 |

^a In 0.1 M DCl-D₂O. ^b py = pyridine; isn = isonicotinamide. ^c Corrected for the comproportionation equilibrium. ^d From the equation¹⁰ $\Delta\nu_{1/2}$ (cm⁻¹) = (2310ν)^{1/2}. ^e From the equation¹⁰ $f = (4.6 \times 10^{-9})\epsilon_{\max}(\Delta\nu_{1/2})$.

**Figure 2.** $[(\text{trans-Ru}(\text{NH}_3)_4\text{py})_2\text{N}(\text{CN})_2]^{4+}$.

at 260 nm for the bis(*trans*-tetraammine isonicotinamide) species is ascribable to the $\pi^* \leftarrow \pi$ transition for the heterocycle. The features at 219 and 350 nm for this complex presumably correspond to those at 223 and 323 nm for the bis(pentaammine) species.

Considering now the oxidized forms, the absorptions at lowest energies can be assigned to ligand-to-metal charge transfer. Such absorption is expected for an anion attached to Ru(III)—vide infra for data on the sulfato complexes. The shift to lower energy as the Ru(III) center becomes more strongly oxidizing (cf. Table III) is in harmony with this assignment. The absorptions at 259 and 277 nm are likely the $\pi^* \leftarrow \pi$ transitions for pyridine and isonicotinamide. These are known to shift to lower energy on oxidizing Ru(II) to Ru(III).

Absorption in the Near-IR Region. The measurements of absorption in the near-IR region were made in 0.1 M DCl in D₂O. Only the mixed-valence species absorb at the longer wavelengths. The results of the measurements done with them are summarized in Table II and for one of the compounds, that based on the *trans*-pyridine complex, are shown in Figure 2. It should be mentioned that the separation of the band in the near-IR from absorption bands at higher energy is particularly clean in the case of the bis(pentaammine-ruthenium) species and the complex is well suited for a detailed study of the properties of the intervalence absorption.

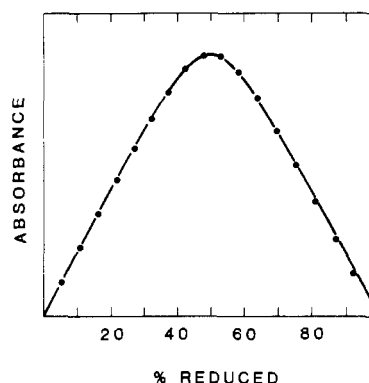
The intervalence absorption band for the bis(pentaammine) species was studied as a function of solvent with the following results (λ_{\max} in nm): D₂O, 1100; acetonitrile, 1275; DMF, 1130; Me₂SO, 1200; acetone, 1220. The results are in reasonable accord with the Hush equation,¹⁰ which shows the energy to vary with $1/n^2 - 1/D$, where n is the refractive index and D the dielectric constant of the medium.

Electrochemical Results. The cyclic voltammetric results for the series of μ -dicyanamide complexes are shown in Table III. For the bis(pentaammine) system, the values of $E_{1/2}$ were shown to be independent of pH over the range 7–0.8. In the particular case of this complex, the two redox stages were well enough separated so that the value of K_{com} could be calculated

Table III. Reduction Potentials and Comproportionation Constants of Dicyanamide-Bridged Binuclear Complexes^a

| Ru moieties ^b | $E_{1/2}$, V vs. NHE | | |
|---|-----------------------|--------------------|------------------|
| | 5+/4+ | 4+/3+ | K_{com} |
| Ru(NH ₃) ₅ | 0.275 | 0.126 | 340 ^d |
| <i>trans</i> -Ru(NH ₃) ₄ py | 0.483 ^c | 0.353 ^c | 155 ^e |
| <i>trans</i> -Ru(NH ₃) ₄ isn | 0.551 ^c | 0.440 ^c | 75 ^e |

^a In 0.1 M HCl. Scan rate = 0.1 V/s. ^b py = pyridine; isn = isonicotinamide. ^c Calculated from the average of the resolved reduction and oxidation wave maxima and the comproportionation constant. ^d Calculated from $E_1 - E_2$ as read directly from the cyclic voltammetry trace. ^e Calculated from the titration data to obtain K_c .

**Figure 3.** Intervalence absorption titration curve for $[(\text{trans-Ru}(\text{NH}_3)_4\text{isn})_2\text{N}(\text{CN})_2]^{5+}$. Titrated in 0.1 M DCl-D₂O with Eu²⁺. [Dimer] = 2.4×10^{-3} M.

directly by reading the two values of $E_{1/2}$ from the cyclic voltammetric trace. Although two waves were discerned in the traces for the other two μ -dicyanamide species, the overlap is so great that the titration procedure⁷ was used to determine K_{com} . The titration results for the *trans*-isonicotinamide complex are shown in Figure 3 along with the fit of the data to the value of K_{com} selected. Titrations were conducted in 0.1 M DCl in D₂O, with [complex] = 2.5×10^{-3} M. Both Eu²⁺ and Ru(NH₃)₆²⁺ were used as reductants, with good agreement between the two sets of results. Subsequent to our experimental work with these systems, the method of treating the electrochemical data for systems showing overlapping cyclic voltammetric waves was developed.¹¹ Our electrochemical data were not obtained in the optimal way for such use, but it is worth noting that the value of K_{com} we calculate from the electrochemical results agree with 5–10% of those determined spectrophotometrically. The value of $E_{1/2}$ for the couple $[\text{Ru}(\text{NH}_3)_5\text{N}(\text{CN})_2]^{2+/+}$ was also determined; it is 0.15 V in 0.1 M HCl and at 25 °C.

Some Properties of the (Sulfato)ruthenium(III) Products. (Sulfato)ruthenium(III) complexes were intermediates in the preparation of some of the binuclear species. The color of these complexes seemed interesting enough to warrant some investigation. Accordingly, the spectra in the UV-visible region were measured with the following results (25 °C 0.1 M HCl): for *trans*-(sulfato)tetraammine(pyridine)ruthenium(III), λ_{\max} (nm) at 331 and 252, with the corresponding values of ϵ (M⁻¹ cm⁻¹) being 3.1×10^3 and 5.0×10^3 ; for the *trans*-isonicotinamide derivatives, $\lambda_{\max} = 345$ and 263 and ϵ is 3.5×10^3 and 5.2×10^3 , respectively. The values of $E_{1/2}$ for the couples based on the general formula *trans*-[Ru(NH₃)₄(SO₄)L]^{1+/0} are 0.20 and 0.29 for L = pyridine and isonicotinamide, respectively, and the respective peak-to-peak separations are 80 and 100 mV. The measurements were done

in 0.1 M HCl at 25 °C and at the rather high scan rate of 5 V s⁻¹ to avoid aquation of the SO₄²⁻ group in the Ru(II) state.

The values of λ_{\max} reported here are in agreement with those of Isied,⁶ which however were obtained on less pure samples. The intense absorptions at lower energy are absent when sulfate is replaced by ammonia. They are assigned as involving sulfate-to-metal charge transfer, an assignment which is supported by the shift to lower energy when the redox potential of the complex increases (vide infra). The absorption bands at higher energy correspond to $\pi^*-\pi$ transitions in the heterocyclic ligands.

Discussion

The studies of bis(ruthenium) complexes based on dicyanamide as bridging group were not significantly complicated by decomposition reactions, at least on the time scale of our experiments. However, it seems certain that valence delocalization is much less complete for the μ -dicyanamide [3,2] species than it is for the analogue with the malononitrile anion as bridging group. The arguments which follow make use of the observations with the bis(pentaammine) complexes, but the conclusion that the μ -dicyanamide species are valence trapped applies with even greater force to the trans-substituted derivatives.

That the electronic coupling is weak in the μ -dicyanamide [3,2] species is indicated by the rather small value of the comproportionation constant, namely, 3.4×10^2 . Much of the stability of the mixed relative to the isovalent state is ascribable to a purely electrostatic effect.⁷ By contrast, when the *tert*-butylmalononitrile anion is the bridging group $K_{\text{com}} > 10^{10}$. The width of the intervalence band at half-height for the μ -dicyanamide molecule is somewhat greater than that calculated from Hush's equation¹⁰ derived for valence-trapped species and a discrepancy in this direction is typical of them. By contrast, the width of the intervalence band at half-height for the μ -[*tert*-butylmalononitrile(1-)] species is less than half the theoretical value.¹ The greatest contrast between the systems is found in the values of the extinction coefficients for the intervalence band: $2.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ for the μ -dicyanamide molecule and $1.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for the μ -[malononitrile(1-)] species. Finally, it is to be noted that the energy of the intervalence band for the μ -dicyanamide molecule is quite sensitive to the dielectric properties of the solvent and that, in contrast to the μ -[malononitrile(1-)] molecule, the energy of the intervalence band varies with $1/n^2 - 1/D$. This implies at once that electron transfer is less rapid than solvent reorientation or less than $\sim 10^{11} \text{ s}^{-1}$. The energy of the intervalence band was not studied as a function of solvent for the trans-substituted derivatives, but the other properties point to the conclusion that they are also valence trapped. The comproportionation constants in fact are lower for them than for the bis(pentaammine) complexes, and the oscillator strengths for the intervalence band are lower; both sets of observations point to the conclusion that the electronic coupling is weaker for the trans-substituted derivatives.

The observations just referred to bear directly on the question of whether the $\pi d-\pi^*$ or $\pi d-\pi$ interaction is dominant in accounting for the metal-to-metal delocalization. For convenience in discussion the properties of the μ -dicyanamide species we have studied are summarized in Table IV. If electronic coupling is enhanced when the value of $E_{1/2}$ increases, this would suggest that $\pi d-\pi$ delocalization provides the dominant coupling mechanism between the metal centers because this would lower the energy of the Ru^{II}[neutral radical]Ru^{II} state relative to the ground state. The dipole strength of the transition is a direct measure of the delocalization, or more precisely of the mixing coefficient:¹⁰ $D = aR$, where D is the dipole strength of the transition, a is the mixing coef-

Table IV. Summary of Properties of Symmetrical Dicyanamide-Bridged Binuclear Complexes

| Ru moiety ^a | $E_{\text{av}},^b$ V vs. NHE | K_{com} | $\lambda_{\text{IT}},$ nm | $10D,^c$ A |
|---|---------------------------------|------------------|------------------------------|------------|
| Ru(NH ₃) ₅ | 0.20 | 340 | 1100 | 9.03 |
| <i>trans</i> -Ru(NH ₃) ₄ py | 0.42 | 155 | 1220 | 8.86 |
| <i>trans</i> -Ru(NH ₃) ₄ isn | 0.50 | 75 | 1250 | 8.53 |

^a py = pyridine; isn = isonicotinamide. ^b $E_{\text{av}} = E(5+/4+) + E(4+/3+)$. ^c Dipole strength $D = [f/(1.085 \times 10^{-5} \nu)]^{1/2}$,¹⁰ where ν is in cm⁻¹.

ficient, and R is metal-metal separation. From Table IV, it is clear that D and therefore a decreases as the Ru(III) becomes more strongly oxidizing, thus suggesting that the Ru(II)-bridging ligand interaction dominates in accounting for the electronic coupling between the metal centers. This is somewhat surprising in view of the negative charge on the ligand but really not more surprising than that CN⁻ acts as a rather strong π acid despite its negative charge.

An examination of the dipole strengths of the ligand-to-metal (LMCT) and metal-to-ligand (MLCT) transitions for the fully oxidized and fully reduced species bears out the conclusion that the Ru(II)- π^* interaction dominates in the case of the μ -dicyanamide species. For it, these values are 0.64 and 1.29 Å respectively for the LMCT and MLCT transitions, while for the μ -[*tert*-butylmalononitrile(1-)] they are 1.79 and 1.24 Å; in both cases the data for the bis(pentaammine) complexes are referred to.

In considering the changes in the comproportionation constant when the auxiliary ligands are changed, the same conclusion is reached for the series under present study as was reached in the examples dealt with earlier;⁷ namely, that for weakly coupled systems such as these, the contribution to the stability of the mixed-valence state by electron delocalization is only a small part of the total effect. After allowance for the statistical factor, the excess stability of the mixed-valence molecule relative to the isovalent state for the Ru(NH₃)₅ system is 1315 cal while for the *trans*-Ru(NH₃)₄py system it is 1070 cal. The decrease in stability attributable to the decrease in electron delocalization, calculated as outlined in ref 7, is 34 cal. The most important factor accounting for the difference of 245 cal is likely the decrease in back-bonding to the bridging ligand when a competing π acid is introduced into the coordination sphere. This in turn decreases the back-bonding stabilization which attends changing from the isovalent to the mixed-valence state.

Not at all understood is the progressive change in the energy of the intervalence transition shown in Table IV. A similar shift of the near-IR absorption to lower energies was reported by Creutz and Taube¹² for the μ -pyrazine species. The values of the band maxima are at 1570, 1650, and 1720 nm as 0, 1, and 2 ammonias on each metal are replaced, the replacing ligands being isonicotinamide and 2,2'-bipyridine in the second and third cases, respectively. These results take on added interest in the light of the observations reported by Callahan and Meyer¹³ for μ -pyrazine-bis[chlorobis(bipyridine)ruthenium](3+) where the band, now characteristic of a valence-trapped species, appears at 1300 nm. The remarkable difference between the Creutz and Taube systems and that studied by Callahan and Meyer cannot be ascribed to the presence of chloride ion. It has been shown¹⁴ that even when chloride ion is replaced by water, the system closely resembles that studied by Callahan and Meyer.

A result of some interest in connection with the absorption spectra of sulfato complexes is that the oscillator strength of

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the LMCT band increases as $E_{1/2}$ for the complex increases. The values of 10^2f for the trans-pyridine and trans-isonicotinamide species are 7.4 and 8.3, respectively. Increasing the strength of the π acid will have two effects: (a) it will tend to contract the π d orbitals and therefore decrease overlap with those of the ligand by withdrawing charge from the metal center and (b) it will decrease the energy gap between the π d and π orbitals. These factors will exert opposing effects on the oscillator strength. In our system, that of factor b is clearly dominant.

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Registry No. [(Ru(NH₃)₅)₂HN(CN)₂](PF₆)₄, 81572-55-6; [(trans-Ru(NH₃)₄py)₂N(CN)₂](ClO₄)₅, 81572-57-8; [(trans-Ru(NH₃)₄isn)₂N(CN)₂](ClO₄)₅, 81572-59-0; trans-[Ru(NH₃)₄(SO₄)py]Cl, 80584-24-3; trans-[Ru(NH₃)₄(SO₄)isn]Cl, 81572-23-8; [Ru(NH₃)₅N(CN)₂](PF₆)₂, 81572-25-0; trans-[Ru(NH₃)₄(SO₂)Cl]Cl, 23346-07-8; [Ru(NH₃)₅H₂O](CF₃SO₃)₃, 53195-18-9; [(Ru(NH₃)₅)₂N(CN)₂]⁵⁺, 81572-26-1; [(trans-Ru(NH₃)₄py)₂N(CN)₂]³⁺, 81572-27-2; [(trans-Ru(NH₃)₄py)₂N(CN)₂]⁴⁺, 81642-83-3; [(trans-Ru(NH₃)₄isn)₂N(CN)₂]³⁺, 81572-52-3; [(trans-Ru(NH₃)₄isn)₂N(CN)₂]⁴⁺, 81642-84-4.

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Ab Initio Study¹ of the Transient Boron Hydrides B₃H₇, B₃H₉, B₄H₈, and B₄H₁₂ and the Fluxional Anion B₃H₈⁻

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The most stable structures of B₃H₇, B₃H₉, B₄H₈, B₄H₁₂, and B₃H₈⁻ are predicted by geometry optimization at the 3-21G basis level with the GAUSSIAN 80 program. At each minimum for a given symmetry, the 6-31G level is extended by polarization on boron (6-31G*) and by correlation at the MP3/6-31G level. Additivity of these two corrections to the 6-31G energy gives the total energy. The most stable structures are C₂2102 for B₃H₇, D_{3h}3003 for B₃H₉, C₁3111 for B₄H₈, D_{4h}4004 for B₄H₁₂, and C_{2v}2102 for B₃H₈⁻. For B₃H₇, C_{2v}1103ST is only 4 kcal/mol less stable; for B₄H₈, C₂2112 and C_{2v}4200 are less stable by 4 and 6 kcal/mol, respectively; and for B₃H₈⁻, C₁1104 is less stable by only 1 kcal/mol.

Introduction

Optimization procedures for locating stationary points on the potential energy surfaces of molecules have advanced considerably in recent years. In addition, the improvements in quality of wavefunctions have included corrections for polarization (e.g., d orbitals on first-row atoms) and for correlation (configuration interaction).³⁻⁵

These corrections are particularly important in those boranes where alternative structures exist in which a terminal hydrogen can become a bridge hydrogen. Electron correlation can more readily be accommodated by the bridge hydrogen because the two electrons of this three-center bond can, with high probability, avoid one another more easily than they can in a two-center terminal bond. More generally, the varieties of bonding situations in the boranes provide further opportunity for effects of both polarization and correlation.

Because of these advances, we felt it would be worthwhile to restudy the structures of the transient hydrides B₃H₇, B₃H₉, B₄H₈, and B₄H₁₂, as well as the fluxional behavior in B₃H₈⁻. In the earlier investigation,⁶ the choice of most stable structure was thought to be sensitive to the completeness of polarization and correlation corrections for B₃H₇. We find here that this is indeed the case. In addition, we felt that the removal of some symmetry constraints in the early study might lead to the prediction of a more stable structure for B₄H₈. This, also, is demonstrated below.

Table I. Relative Energies (kcal/mol) at 6-31G, Increments to 6-31G* and MP3/6-31G, and Estimated MP3/6-31G* Relative Energies

| species | fig | styx ^a | 6-31G | increment 6-31G* | increment MP3/ 6-31G | est MP3/ 6-31G* |
|---|-----|-------------------------------------|-------|---------------------|----------------------------|-----------------------|
| B ₃ H ₇ | 1a | C _{2v} 1103ST ^b | -5.4 | 3.9 | 5.9 | 4.4 |
| | 1b | C _{2v} 1103EC | 8.2 | 2.9 | 4.5 | 15.6 |
| | 1c | C _{2v} 1103EC | 7.3 | 2.5 | 3.4 | 13.2 |
| | 1d | C _{2v} 2102 | -5.3 | 3.5 | 9.2 | 7.4 |
| | 1e | C _{2v} 2102 | 0 | 0 | 0 | 0 |
| B ₄ H ₈ | 3a | C _{2v} 4020 | 10.1 | -1.2 | -3.2 | 5.7 |
| | 3b | C _{2v} 0204ST | -1.1 | 8.6 | 14.8 | 22.3 |
| | 3c | C _{2v} 1113 | -12.8 | 9.6 | 16.2 | 13.0 |
| | 3d | C _{2v} 2112 | -7.0 | 4.8 | 6.4 | 4.2 |
| | 3e | C ₁ 3111 | 0 | 0 | 0 | 0 |
| B ₃ H ₈ ⁻ | 4a | C _{2v} 1104 | -1.2 | 0.5 | 1.5 | 0.8 |
| | 4b | C _{2v} 2013 | 0 | 0 | 0 | 0 |
| B ₂ H ₆ ^c | | D _{2h} 2002 | -13.7 | -6.6 | -15.2 | -35.5 |
| B ₃ H ₉ ^c | | D _{3h} 3003 | -0.4 | -5.1 | -25.9 | -31.4 |
| B ₄ H ₁₂ ^c | | D _{4h} 4004 | 6.1 | 0.9 | -28.0 | -21.0 |

^a The symmetry is given first and then the numbers are *s* for bridge hydrogens, *t* for three-center BBB bonds, *y* for single bonds, and *x* for each additional terminal H on a BH unit. ^b ST and EC refer to staggered or eclipsed orientations of BH₂ relative to the remainder of the molecule. See ref 6. ^c Energies are relative to separated BH₃ units.

Methods

For each substance, the few or several structures were geometry optimized, with or without symmetry constraints as indicated below. The GAUSSIAN 80 program⁷ was used in the 3-21G basis⁸ in order to provide efficient calculation of ana-

(1) For convenience, the abbreviations in this paper are collected here: 6-31G, 6 Gaussians to inner shell, 3 Gaussians plus one with different exponent for valence shell; DZ, double- ζ calculation equivalent to 6-31G; 6-31G* adds polarization (d orbitals) to nonhydrogen atoms; PRDDO, partial retention of diatomic differential overlap; ST, staggered; EC, eclipsed.

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