

The adjacent 711-cm<sup>-1</sup> band, which is slightly D<sub>2</sub>O sensitive, is also present in Cu<sup>III</sup>TG, and is assigned to  $\delta_{C=O}$ .<sup>18,19</sup> The group of bands between 890 and 1130 cm<sup>-1</sup> are thought to be skeletal modes of uncertain composition.<sup>17</sup>

**Acknowledgment.** We thank Dr. Dennis Evans for a gift of Vycor tubing for construction of the electrolysis cell. During this work J.R.K. held a National Institutes of Health National Research Service Award 1 F32 HL05093. This work was supported by NIH Grant GM13498.

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Received May 23, 1977

## Trimethylsulfonium Ion as a Ligand: Synthesis and Characterization of [(NH<sub>3</sub>)<sub>5</sub>RuS(CH<sub>3</sub>)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub>

Sir:

The instances in which a ligand carrying positive charge on the donor atom displaces a donor atom bearing negative charge from a metal ion are rare. We wish to report what we believe to be the first example of the formation of a complex of

**Table I.** Absorption Spectra for Pentaammineruthenium(II) Complexes of Sulfur Ligands

(CH <sub>3</sub> ) <sub>2</sub> S	$\lambda_{\max}$ ( $\epsilon$ )	
	(CH <sub>3</sub> ) <sub>2</sub> SO	(CH <sub>3</sub> ) <sub>3</sub> S <sup>+</sup>
358 (64)	313 (240)	320 (235)
258 (2100) <sup>a</sup>	210 (2600)	210 (7500)
235 (2050) <sup>a</sup>		

<sup>a</sup> Reference 1.

**Table II.** <sup>1</sup>H NMR Chemical Shifts for Protons in Ru(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup> Complexes and in the Free Hetero Ligands

	S(CH <sub>3</sub> ) <sub>2</sub>		(CH <sub>3</sub> ) <sub>2</sub> SO		S(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>		CO
	Free <sup>a</sup>	Bound <sup>a</sup>	Free	Bound	Free	Bound	
CH <sub>3</sub>	2.06	2.06	2.7 <sup>b</sup>	3.28 <sup>b</sup> (3.4) <sup>c</sup>	2.84 <sup>a</sup>	3.4 <sup>c</sup>	
<i>cis</i> -NH <sub>3</sub>		2.2		2.4 <sup>c</sup>		2.5 <sup>c</sup>	2.6 <sup>d</sup>
<i>trans</i> -NH <sub>3</sub>		3.0		3.6 <sup>c</sup>		3.9 <sup>c</sup>	3.7 <sup>d</sup>

<sup>a</sup> Reference 1. <sup>b</sup> C. V. Senoff, E. Maslowsky, and R. G. Goel, *Can. J. Chem.*, **49**, 3585 (1971). <sup>c</sup> This work. <sup>d</sup> Reference 9.

S(CH<sub>3</sub>)<sub>3</sub><sup>+</sup> with a metal ion by a net substitution reaction and, in fact, the first example of a sulfonium ion complex. The species (NH<sub>3</sub>)<sub>5</sub>RuS(CH<sub>3</sub>)<sub>3</sub><sup>3+</sup> (I) was synthesized as follows. Acetone (500 mL) was deaerated with argon for a minimum of 5 h in a gas scrubbing tower. To the outlet of the tower was attached a 10-mL reaction vessel which was simultaneously deaerated and then charged with 7 mL of acetone and, typically, 100 mg (4.30 × 10<sup>-4</sup> mol) of [(CH<sub>3</sub>)<sub>3</sub>S]PF<sub>6</sub>. After 0.5 h of continuous argon bubbling, 234 mg (4.73 × 10<sup>-4</sup> mol) of freshly prepared [(NH<sub>3</sub>)<sub>5</sub>RuH<sub>2</sub>O](PF<sub>6</sub>)<sub>2</sub> was added. The reaction mixture was shielded from light and the argon flow was continued for 16 h. A very slow color change from deep orange to pale yellow was observed. The solution was poured into ether and filtered and the residue was dissolved in a minimum (1-2 mL) of 0.1 M HCl and filtered. Solid NH<sub>4</sub>PF<sub>6</sub> was then added until precipitation of the very pale yellow salt commenced. Anal: Calcd for C<sub>3</sub>H<sub>24</sub>N<sub>5</sub>SRuP<sub>3</sub>F<sub>18</sub>: C, 5.16; H, 3.46; N, 10.03; Ru, 14.50; S, 4.59; F, 48.97. Found: C, 5.44; H, 3.39; N, 9.53; Ru, 14.5; S, 4.9; F, 47.1. The yield was 25%.

The salient features of UV-vis spectrum of I are summarized in Table I. The similarity to the spectrum of the (NH<sub>3</sub>)<sub>5</sub>RuSO(CH<sub>3</sub>)<sub>2</sub><sup>2+</sup> ion<sup>1</sup> is apparent. In both cases, the lowest energy bands are d-d transitions, while those at 210 nm are ligand centered.

A 60-MHz NMR spectrum taken in 0.24 M DCl or Me<sub>2</sub>SO-*d*<sub>6</sub> revealed three peaks with areas in the ratio of 4:3:1 corresponding to the protons located on the *cis*-ammine, methyl, and *trans*-ammine groups, respectively (see Table II). The ammine protons appear as broad peaks, while the methyl protons appear as a sharp singlet. It should be noted that each of the ligands (CH<sub>3</sub>)<sub>2</sub>S, (CH<sub>3</sub>)<sub>3</sub>S<sup>+</sup>, and CO produce downfield shifts in the *trans* relative to the *cis* ammonia ligands.

The NH<sub>3</sub> symmetric deformation frequencies occur in the infrared at 1292 (s), 1305 (w), and 1318 and 1328 cm<sup>-1</sup> (s). In compounds containing the (NH<sub>3</sub>)<sub>5</sub>Ru<sup>II</sup> or (NH<sub>3</sub>)<sub>5</sub>Ru<sup>III</sup> ion, this vibrational mode would characteristically occur either in the range 1260-1290 or 1330-1360 cm<sup>-1</sup>.<sup>2</sup> A similar effect is manifested in some compounds such as [(NH<sub>3</sub>)<sub>5</sub>RuNO]Br<sub>3</sub> which contain NO<sup>+</sup> bound to Ru<sup>II</sup> ( $\delta_{\text{NH}_3}$  1310 cm<sup>-1</sup>).<sup>3</sup>

Cyclic voltammograms were recorded in dry acetonitrile containing 0.1 M (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NPF<sub>6</sub> as a supporting electrolyte or in 0.1 M HCl. In acetonitrile, a wave was observed at +1460 mV vs. SCE in the oxidation mode, but no corresponding reduction wave. On repeated cycling this wave disappeared with concomitant development of a reversible wave at +415 mV vs. SCE which corresponds to the [(NH<sub>3</sub>)<sub>5</sub>RuNCCH<sub>3</sub>]<sup>3+/2+</sup> redox couple.<sup>4</sup> In 0.1 M HCl, an irreversible (in the sense described above) wave was seen at 1250 mV vs. NHE which disappeared on repeated cycling producing the [(NH<sub>3</sub>)<sub>5</sub>RuCl]<sup>2+</sup> ion. The large positive redox potential is characteristic of complexes of Ru<sup>II</sup> containing ligands, which are strong  $\pi$  acids and indifferent  $\sigma$  donors, and is evidence for metal to ligand back bonding. In any case, it is impossible to understand the affinity of Ru<sup>II</sup> for S(CH<sub>3</sub>)<sub>3</sub><sup>+</sup> on the basis of a simple  $\sigma$ -bond interaction.

It seems worth-while to point out explicitly that, although within a carefully defined series, there may be a relation between the position of the  $\pi$ -d- $\pi^*$  absorption and the affinity of the  $\pi$ -acid ligand for the metal ion, there is certainly no mo-

notonous relationship when all  $\pi$ -acid ligands are considered. By way of example, the cases of CO and pyridine can be compared. The affinity of the former ligand is certainly greater than that of the latter.<sup>6,7</sup> The pyridine complex of pentaaminerruthenium(II) has a very strong absorption with a maximum at 407 nm,<sup>8</sup> while no absorptions of the CO duplex are observed at wavelengths above 210 nm which are not ascribable to d-d transitions (weak absorption in the 270–280 range).<sup>9</sup>

**Acknowledgment.** Financial support of this research by the National Institutes of Health Grant No. GM13638 is gratefully acknowledged.

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Received September 12, 1977

### 1,9-Dimethyldibenzo[*b,f*]pentalene Dication and Dianion. New $14\pi$ and $18\pi$ Aromatic Systems

Sir:

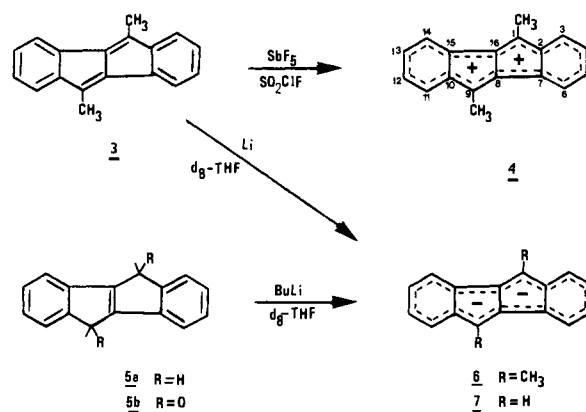
Fused conjugated systems containing  $4n\pi$  electrons, similar to the monocyclic cyclooctatetraene<sup>1</sup> and [12]annulene,<sup>2</sup> may in principle acquire aromaticity by oxidation to the corresponding dication, or by formation of the dianion. These ions are predicted to behave like peripheral aromatic systems containing  $(4n + 2)\pi$  electrons.<sup>3</sup> The pentalene dianion,<sup>4</sup> heptalene dianion,<sup>5</sup> and dibenzononalene dianion<sup>6</sup> were prepared and exhibited aromatic character. The preparation of **2**, the  $8C-6\pi$  aromatic dication of the unknown pentalene (**1**) has proved to be unusually difficult: several attempts to



prepare derivatives of **2** by chemical or electrochemical methods proved to be unsuccessful.<sup>7</sup> The difficulties in preparing derivatives of **2** were interpreted in terms of steric hindrance to delocalization in protonated dibenzo[*cd,gh*]-

pentalenequinone<sup>7a</sup> and partial antiaromatic character of the cyclopentadiene cation moieties.<sup>7c</sup> We wish to report the preparation and characterization of the benzannulated pentalene dication and dianion and to show that the system may acquire aromaticity by conversion either to the dication or dianion.

Upon treatment of 1,9-dimethyldibenzo[*b,f*]pentalene (**3**)<sup>8</sup> with  $SbF_5$  in  $SO_2ClF$  at  $-78^\circ C$ , the two-electron oxidation product 1,9-dimethyldibenzo[*b,f*]pentalene dication (**4**) was obtained. The  $^1H$  NMR spectrum (Table I) of the dark green solution consists of two triplets at 9.72 and 9.40 ppm attributed to  $H_4, H_5, H_{12},$  and  $H_{13}$  and two doublets at 9.84 and 9.49 ppm attributed to  $H_3, H_6, H_{11},$  and  $H_{14}$ . No spectral change was noted over the temperature range  $-40$  to  $0^\circ C$ .



The observed average proton downfield shift accompanying the transformation  $3 \rightarrow 4$  is 2.8 ppm. It was shown in a series of charged aromatic molecules that the  $^1H$  chemical shifts are a linear function of the electron density.<sup>9</sup> On this basis, the average proton downfield shift  $\Delta\delta$  accompanying the oxidation process  $3 \rightarrow 4$  is expected to be 1.4 ppm. The observed chemical shifts difference is significantly enhanced (by 1.4 ppm) and is attributable to the formation of a diamagnetic ring current. Noteworthy is the deshielding observed in the chemical shift of the aromatic protons indicating the delocalization of all  $14\pi$  electrons in **4**. The chemical shifts of the methyl substituents (4.08 ppm) correlate nicely to other methyl derivatives of dicationic species.<sup>1a,10</sup>

Further support to the dicationic nature of **4** is obtained by comparison of the  $^{13}C$  NMR of **3** and **4**. Oxidation of **3** resulted in a significant downfield shift. The observed average  $^{13}C$  chemical shift  $\Delta\delta_c$  in the transformation  $3 \rightarrow 4$  is  $\sim 368$  ppm or 184 ppm/e. This value is very near to that observed for other polycyclic dications<sup>1b,11</sup> which is very similar indeed to the magnitude predicted by the Spiescke-Schneider relationship.<sup>9a,12</sup> The resonances of the fused benzene carbon atoms appear at a considerably lower field than those in **3**; hence delocalization of all  $14\pi$  electrons, as deduced by  $^1H$  NMR is occurring.

Treatment of **3** with lithium wire or deprotonation of 1,9-dihydrodibenzo[*b,f*]pentalene (**5a**)<sup>13</sup> with  $BuLi$  in  $THF-d_8$  yielded dianions **6** and **7**, respectively.<sup>14</sup> The  $^1H$  NMR spectra

Table I.  $^1H$  NMR Parameters for Dibenzof[*b,f*]pentalene Dication, Dianions, and Related Compounds<sup>a</sup>

	$H_3, H_6, H_{11}, H_{14}$	$H_4, H_5, H_{12}, H_{13}$	R
<b>3</b> <sup>b</sup>		7.12 (m), 6.89 (m)	2.17 (s) <sup>c</sup>
<b>4</b> <sup>d</sup>	9.84 (d, $J = 9$ Hz), 9.49 (d, $J = 8$ Hz)	9.72 (t, $J = 7.6$ Hz), 9.40 (t, $J = 7$ Hz)	4.08 (s) <sup>c</sup>
<b>5</b> <sup>b</sup>		7.25 (m)	3.53 (s) <sup>e</sup>
<b>6</b> <sup>f</sup>	7.57 (d, $J = 7$ Hz), 7.27 (d, $J = 8$ Hz)	7.17 (t, $J = 7$ Hz), 6.91 (t, $J = 8$ Hz)	3.10 (s) <sup>c</sup>
<b>7</b> <sup>f</sup>	7.65 (d, $J = 8$ Hz), 7.24 (d, $J = 8$ Hz)	6.80 (dd, $J_1 = 8$ Hz, $J_2 = 6$ Hz), 6.54 (dd, $J_1 = 8$ Hz, $J_2 = 7$ Hz)	5.90 (s) <sup>e</sup>

<sup>a</sup> Chemical shifts are in  $\delta$  (parts per million) from  $Me_4Si$  in a capillary. <sup>b</sup> In  $CDCl_3$  solution at  $32^\circ C$ . <sup>c</sup> Bruker WH-270 of the Weizmann Institute of Science, Rehovot, Israel. <sup>d</sup> In  $SO_2ClF-SbF_5$  solution using acetone- $d_6/Me_4Si$  capillary at  $-78^\circ C$ . <sup>e</sup> Varian HA 100 D. <sup>f</sup> In  $THF-d_8$  solution.