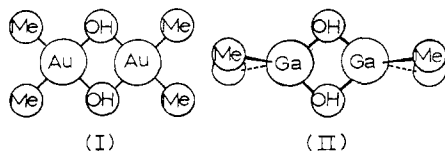


solutions. The equilibrium constant for the dimerization process  $2(\text{CH}_3)_2\text{Ga}(\text{OH})(\text{OH}_2) = (\text{CH}_3)_2\text{Ga}(\text{OH})_2\text{-Ga}(\text{CH}_3)_2 + 2\text{H}_2\text{O}$  is  $\log K_d = \log (*\beta_{22}/*\beta_{11}^2) = 2.57 \pm 0.02$ . This value is rather typical for such dimerization processes which generally have equilibrium constants of *ca.*  $10^3$  and which appear to be relatively insensitive to the charge on the dimerizing species. The corresponding value for  $2(\text{CH}_3)_2\text{SnOH}^+(\text{aq}) = (\text{CH}_3)_2\text{Sn}(\text{OH})_2\text{Sn}(\text{CH}_3)_2^{2+}(\text{aq})$  is  $\log K_d = 2.48 \pm 0.02$ .<sup>14,19</sup>

The high stability of these binuclear (2:2) dimethyl-gold and -gallium(III) complexes in solution is surprising. If they have the di- $\mu$ -hydroxo-bridged structures I and II, normal metal-oxygen bond lengths



would lead to short metal-metal distances. Indeed, it is on this basis that the formation of the tetrameric hydroxides observed in the solid state is rationalized. Dimethylgallium chloride, bromide, and iodide are all dimeric molecules,<sup>20</sup> while the fluoride has been found in tri-<sup>21</sup> and tetrameric forms.<sup>22</sup>

Oxygen-bridged species with structures analogous to that suggested for the dimeric hydroxide have been proposed for both trimethylsiloxydimethylgallium(III)<sup>23</sup> and trimethylsiloxydimethylgold(III)<sup>24</sup> which are

(19) R. S. Tobias and M. Yasuda, *J. Phys. Chem.*, **68**, 1820 (1964).

(20) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 1, 3rd ed, Methuen and Co. Ltd., London, 1967, p 355.

(21) H. Schmidbauer, J. Weidlein, H.-F. Klein, and K. Eiglmeier, *Chem. Ber.*, **101**, 2268 (1968).

(22) H. Schmidbauer and H.-F. Klein, *ibid.*, **101**, 2278 (1968).

(23) H. Schmidbauer, *Angew. Chem.*, **77**, 189 (1965).

(24) H. Schmidbauer and M. Bergfeld, *Inorg. Chem.*, **5**, 2069 (1966).

dimeric in organic solvents. In the case of trimethylsiloxydimethylaluminum(III), the presence of the four-membered ring has been verified by an X-ray structure determination.<sup>25</sup> With dimethylgallium hydroxide, it appears that the enthalpy change for polymerization-depolymerization is small, so that the particular molecular form isolated in the solid will be influenced by packing considerations in the crystal. The absence in aqueous solution of larger polymers such as the tetramers is not surprising, for their solubility should be very low.

The particular stability of the uncharged hydroxo complex is emphasized in both the  $(\text{CH}_3)_2\text{Ga}^{\text{III}}$  and  $(\text{CH}_3)_2\text{Au}^{\text{III}}$  cases by the fact that the  $n(\log [\text{H}^+])$  curves approach  $\bar{n} = 1$  asymptotically. Only at much higher pH values will the solid hydroxides  $[(\text{CH}_3)_2\text{AuOH}]_4$  and  $[(\text{CH}_3)_2\text{GaOH}]_4$  dissolve to give anionic species.

Coordination of two methyl groups to Ga(III) has several important effects. First, it is likely that the coordination number for gallium changes from the value of 6 which is known to be the hydration number of  $\text{Ga}^{3+}$  to 4 (two  $\text{CH}_3$ , two  $\text{H}_2\text{O}$ ). Second, the rate of exchange of bound and bulk water is greatly increased by the presence of the two methyl groups. Finally, the acidity is greatly reduced. Solutions of  $\text{Ga}^{3+}$  are highly hydrolyzed and equilibria are attained only very slowly.<sup>26</sup>

**Acknowledgment.**—We wish to express our appreciation to the Italian National Research Council (CNR) for a fellowship awarded to L. P.

(25) P. J. Wheatley, *J. Chem. Soc.*, 2562 (1963).

(26) H. R. Craig and S. Y. Tyree, Jr., *Inorg. Chem.*, **8**, 591 (1969).

## Notes

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### Structural and Spectroscopic Characteristics of the Nonachlorodirrhodate(III) Anion

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During a general investigation of the extraction of the group VIII metals as anionic complexes by long-chain quaternary ammonium compounds,<sup>1</sup> the extraction of rhodium(III) from an aqueous chloride solution was attempted. Since excess chloride ion was present, the anticipated extracted species was

(1) M. L. Good and S. C. Srivastava, *J. Inorg. Nucl. Chem.*, **27**, 2429 (1965), and references cited therein.

hexachlororhodate(III); however the observed visible spectrum was unlike that reported for this species or any other octahedral aquochloro complex reported by Kleinberg and coworkers.<sup>2</sup> In an attempt to identify the extracted species, several solid, short-chain quaternary ammonium chloride-rhodium(III) chloride compounds were prepared. The subsequent investigation yielded the results reported here.

#### Experimental Section

**Extraction.**—Aqueous solutions of either sodium hexachlororhodate(III) or rhodium trichloride trihydrate were extracted with a benzene solution of "Aliquat-336."<sup>3</sup> The organic layer was separated and dried for at least 24 hr over silica gel. Varying concentrations of all reagents mentioned above were used

(2) W. C. Wolsey, C. A. Reynolds, and J. Kleinberg, *Inorg. Chem.*, **2**, 463 (1963).

(3) "Aliquat-336," subsequently referred to as A-336, is a mixture of long-chain, C<sub>8</sub>-C<sub>16</sub>, substituted quaternary ammonium chlorides consisting mainly of tricaprolylmonomethylammonium chloride obtained from General Mills.

and no change in the nature of the resulting extracted species could be observed.

In addition, the same species could be obtained by stirring either the solid hexachloro salt or the trichloride trihydrate with a benzene solution of the quaternary chloride. The solution which resulted after removal of the excess solid was indistinguishable from the extracted species prepared above.

**Compounds.**  $[(C_2H_5)_4N]_3Rh_2Cl_9$  was prepared by the method described by Fraenkel.<sup>4</sup> Stoichiometric amounts of tetraethylammonium chloride and rhodium trichloride trihydrate were dissolved in a minimum amount of concentrated hydrochloric acid. Upon mixing, the product precipitated. *Anal.* Calcd for  $[(C_2H_5)_4N]_3Rh_2Cl_9$ : Cl, 34.9; Rh, 22.5. Found: Cl, 34.2; Rh, 22.5.

$[(C_2H_5)_4N]_3Cr_2Cl_9$  was prepared as described by Adams.<sup>5</sup> One gram each of tetraethylammonium chloride and chromium chloride was stirred in thionyl chloride for 24 hr. The product precipitated as it was formed. *Anal.* Calcd for  $[(C_2H_5)_4N]_3Cr_2Cl_9$ : Cl, 39.3; Cr, 12.6. Found: Cl, 38.9; Cr, 12.7.

$(NH_4)_3RhCl_6$ ,  $RhCl_3 \cdot 3H_2O$ , and  $Na_3RhCl_6 \cdot 12H_2O$  were purchased and used without further purification from K & K Laboratories, Matthey Bishop, and Matthey Bishop, respectively.

$K_2RhCl_5(H_2O)$  was prepared by the addition of stoichiometric amounts of rhodium trichloride trihydrate and potassium chloride to water containing a few drops of hydrochloric acid. Upon evaporation of excess solvent, the product precipitated. The purity of the product was ascertained by comparison of its ligand field spectrum with that reported in the literature.<sup>2</sup>

**Electronic Spectral Measurements.**—The visible spectra of both the extract and the solids were recorded on a Perkin-Elmer Model 450 spectrophotometer. The spectra of the solids were obtained on filter paper as Nujol mulls and the solution spectra were obtained in matched quartz cells of 1-cm path length. Benzene solutions of about  $10^{-3}$  M  $[A-336]_3Rh_2Cl_9$  were used to obtain the molar absorptivities reported.

**Infrared Spectral Measurements.**—The far-infrared spectra of both the extract and the solids were taken in the region 400–150  $cm^{-1}$  on a Beckman IR-11 far-infrared spectrophotometer. The solids were run as Nujol mulls between polyethylene plates and the extracts were placed in a 2-mm polyethylene cell.

**X-Ray Analysis.**—X-Ray powder diffraction photographs were taken of finely powdered samples mounted in thin-walled 0.3-mm Pyrex capillaries using a 11.5-cm Debye-Scherrer camera with Ni-filtered Cu K $\alpha$  radiation ( $\lambda$  1.5418 Å).

## Results and Discussion

The observed absorption maxima of the ligand field spectra along with the appropriate molar absorptivities for pertinent solutions and solids are listed in Table I. A comparison of the electronic spectra of the extracted species with those reported by Kleinberg, *et al.*,<sup>2</sup> indicated that the extracted species was not a normal octahedral chloroaquo complex of rhodium(III). A search of the literature revealed that several other rhodium-chloro complexes had been previously prepared using short-chain quaternary ammonium cations.<sup>4</sup>

The complex compound tetraethylammonium nonachlorodirrhodate(III),  $[(C_2H_5)_4N]_3Rh_2Cl_9$ , was prepared by the procedure of Fraenkel and the ligand field spectrum was taken. The resulting spectrum was indistinguishable from that obtained for the extracted species in benzene solution. Ivanova, *et al.*,<sup>6</sup> performed a similar extraction using the tetra-*n*-octyl-

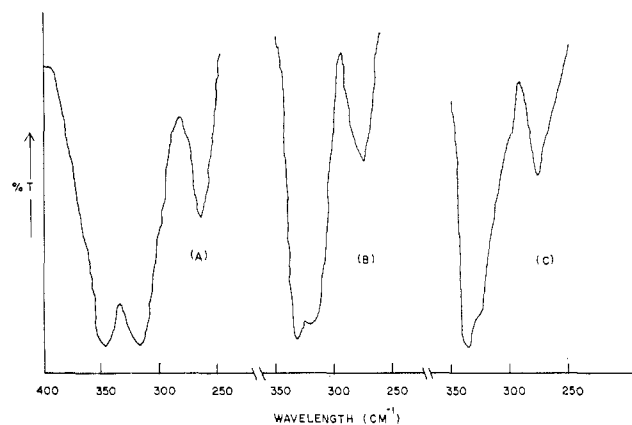


Figure 1.—Infrared spectra of (A)  $[(C_2H_5)_4N]_3[Cr_2Cl_9]$  in Nujol mull, (B)  $[(C_2H_5)_4N]_3[Rh_2Cl_9]$  in Nujol mull, and (C)  $[A-336]_3[Rh_2Cl_9]$  in benzene solution.

ammonium cation to extract rhodium(III) from water into nitrobenzene and reported that the stoichiometry of the extracted species was  $[(C_8H_{15})_4N]_{1.5}Rh_{1.0}Cl_{4.41}$ . Their reported ligand field spectrum is consistent with the results presented here in Table I for  $[(C_2H_5)_4N]_3Rh_2Cl_9$  and the extracted species.

TABLE I  
LIGAND FIELD SPECTRAL DATA

Species	$\lambda_{max}$ , $m\mu$	$\epsilon^a$	Ref	Solvent
$Rh(H_2O)_6^{3+}$	311, 396	67.4, 62.0	c	Water
$RhCl(H_2O)_5^{3+}$	335, 426	50.0, 50.4	c	Water
$RhCl_2(H_2O)_4^+$	349, 450	49.5, 64.9	c	Water
<i>cis</i> - $RhCl_3(H_2O)_3$	376, 474	93.5, 68.3	c	Water
<i>trans</i> - $RhCl_3(H_2O)_3$	370, 471	71.6, 77.1	c	Water
$RhCl_4(H_2O)_2^-$	385, 488	54.1, 72.0	c	Water
$RhCl_5(H_2O)^{2-}$	402, 507	73.4, 72.8	c	Water
$RhCl_6^{3-}$	411, 518	93.8, 111.5	c	Water
$Rh_2Cl_9^{3-}$	435, 540 <sup>b</sup>	308.8, 98.0	d	Benzene
$Rh_2Cl_9^{3-}$	442, 546	...	b	Nitrobenzene

<sup>a</sup> Beer's law was used for calculation of molar absorptivities. <sup>b</sup> A weak absorption maximum reported at 340  $m\mu$  by Ivanova was not observed: S. N. Ivanova, L. M. Gindin, and L. Ya. Mironova, *Zh. Neorgan. Khim.*, **12**, 1638 (1967). <sup>c</sup> See ref 2. <sup>d</sup> This work.

TABLE II  
FAR-INFRARED SPECTRAL DATA

Species	$\nu$ , $cm^{-1}$ <sup>a</sup>	Ref
$[(C_2H_5)_4N]_3[Cr_2Cl_9]$ (solid)	345 s, 319 s, 265 m, 341 s, 322 s	b, c
$[(C_2H_5)_2NH_2]_3[Cr_2Cl_9]$ (solid)	350 s, br, 322 s, b, 270 m	d
$[(C_2H_5)_4N]_3[Rh_2Cl_9]$ (solid)	331 s, 319 s, 277 m	b
$[NH_4]_3[RhCl_6]$ (solid)	338 s, 326 sh, 205 s	b, e
$[A-336]_3[Rh_2Cl_9]$ (extract)	332 s, 322 sh, 276 m	b
$K_2[RhCl_5(H_2O)]$ (solid)	337 sh, 322 s	b, f

<sup>a</sup> Abbreviations: s, strong; m, medium; sh, shoulder; br, broad. <sup>b</sup> This work. <sup>c</sup> Reference 5. <sup>d</sup> P. C. Crouch, G. W. A. Fowles, and R. A. Walton, *J. Chem. Soc., A*, 972 (1969). <sup>e</sup> A weak band at 160  $cm^{-1}$  was observed but not assigned as a vibration of the complex. <sup>f</sup> A broad band was observed in the region  $\sim 175$ –110  $cm^{-1}$  of medium intensity which we do not assign as a vibrational mode of the complex.

To obtain structural information about the new rhodium(III) species, the vibrational spectrum was obtained and compared to the spectra of other possibly related complexes (see Table II). The far-infrared

(4) O. v. Fraenkel, *Monatsh.*, **85**, 119 (1923), and references cited therein.

(5) D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *J. Chem. Soc.*, 2189 (1963).

(6) See footnote b, Table I.

TABLE III  
 X-RAY POWDER PHOTOGRAPHIC DATA

[(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N] <sub>3</sub> [Cr <sub>2</sub> Cl <sub>9</sub> ]		[(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N] <sub>3</sub> [Rh <sub>2</sub> Cl <sub>9</sub> ]	
<i>d</i> , Å	Rel intens <sup>a</sup>	<i>d</i> , Å	Rel intens <sup>a</sup>
11.3	4	11.3	4
9.53	2	...	...
8.638	8	8.514	8
8.014	1	7.978	1
5.641	3	5.641	3
4.925	6	4.904	6
4.509	1	4.475	1
4.244	1	4.268	1
4.022	4	3.995	4
3.743	2	3.719	2
3.404	1	3.372	1
3.263	1	...	...
3.215	1	3.209	1
3.027	1	3.041	1
2.835	3	2.816	3
2.650	1	2.660	1
2.408	1	2.411	1
2.286	2	2.280	2
2.205	1	2.213	1
2.110	1	2.117	1
1.991	10	1.987	10
1.733	7	1.728	7
1.239	3	1.238	3

<sup>a</sup> Relative intensities range 1–10, 10 being most intense.

absorption maxima which were observed in the region 150–400 cm<sup>-1</sup> for the extracted species and for tetraethylammonium nonachlorodirrhodate(III) are the same within the limit of error of the method. In addition, the observed spectra consist of the same number of bands of the same relative intensity and position as those of the complex tetraethylammonium nonachlorodichromate(III). In an early paper by Adams, *et al.*,<sup>5</sup> this chromium complex was prepared and the far-infrared spectrum was taken. These workers observed only two maxima. The higher frequency band was assigned as the "terminal" chromium–chlorine stretching mode and the lower as the "bridged" chromium–chlorine stretching mode. These assignments were made on the basis of the X-ray analysis performed by Wessel and Ijdo<sup>7</sup> which indicated that the complex ion consists of two distorted octahedra sharing a face. Recently, Walton, *et al.*,<sup>8</sup> reported new far-infrared data which substantiate the results reported here. These workers observed three distinct bands, an intense doublet and a band of medium intensity of lower frequency. An ion of the type M<sub>2</sub>Cl<sub>9</sub><sup>n-</sup> of D<sub>3h</sub> symmetry is expected to have two "terminal" stretching modes and two "bridged" stretching modes. However, only three bands are observed for both the rhodium and the chromium complex. In the case of chromium, the absent band, a "bridged" stretching band, is thought either to be obscured by the terminal stretching bands or to occur at a frequency lower than 200 cm<sup>-1</sup>.<sup>8</sup> For the rhodium complex, it seems unlikely that this absent band is below 150 cm<sup>-1</sup> since the "bending" mode for RhCl<sub>6</sub><sup>3-</sup> is found at 205 cm<sup>-1</sup>. The only reasonable alternative is that

it is obscured by one of the "terminal" stretching modes. It should also be noted that no bands are observed in the "bridged" stretching region (~270 cm<sup>-1</sup>) for either RhCl<sub>6</sub><sup>3-</sup> or RhCl<sub>5</sub>(H<sub>2</sub>O)<sup>2-</sup>, the other probable products. In Figure 1 the spectra of the chromium and rhodium complexes as well as that of the extract are shown for comparison. Note the remarkable similarity between the three spectra. The greater splitting of the doublet for the solid nonachlorodirrhodate(III) ion as compared to the extracted species may be attributed to lowering of the symmetry of the complex ion in the crystal lattice due to its site symmetry, while in the solution no such restrictions are placed on the ion pair formed.

As further evidence of the structure of this complex ion, X-ray diffraction powder photographs of the two compounds, tetraethylammonium nonachlorodirrhodate(III) and tetraethylammonium nonachlorodichromate(III), were taken. A comparison of the powder patterns indicated that the two compounds were isomorphous (see Table III).

This information is completely consistent with the basic structure assigned by Wessel and Ijdo<sup>7</sup> for Cr<sub>2</sub>Cl<sub>9</sub><sup>3-</sup>; that is, two pyramidally distorted octahedra sharing a face.

**Acknowledgments.**—The X-ray equipment used to obtain crystal powder photographs was purchased under NIH Grant No. GM-08348. The authors wish to thank Tulane University for the use of their Beckman IR-11 purchased partially by funds from National Science Foundation under Grant No. 28709. The original extraction work was begun under AEC Contract No. AT(40-1)-2576.

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### Formation Constants of Substituted Pyridine Complexes of Cadmium(II) and Mercury(II) $\alpha, \beta, \gamma, \delta$ -Tetraphenylporphin. The Hammett $\rho$ as a Measure of Cation Polarizing Ability

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We have previously shown<sup>2</sup> that zinc(II)  $\alpha, \beta, \gamma, \delta$ -tetraphenylporphin (ZnTPP) forms only 1:1 complexes in solution with a variety of substituted pyridine ligands and that their proton magnetic resonance spectra exhibit exchange-averaged patterns and chemical shifts similar to those of the MgTPP adducts. The stability constants for the ZnTPP reactions show both log  $K$ -p*K*<sub>a</sub> and Hammett-type correlations.

We now report stability constants for the formation

(1) (a) Abstracted from the Ph.D. Thesis of C. H. K., Howard University, 1969. (b) To whom inquiries concerning this work should be addressed.

(2) C. H. Kirksey, P. Hambright, and C. B. Storm, *Inorg. Chem.*, **8**, 2141 (1969).

(7) G. J. Wessel and D. J. W. Ijdo, *Acta Cryst.*, **10**, 466 (1957).

(8) See footnote *d*, Table II.