

Figure 3. $\text{Na}_{0.50}\text{VOPO}_4 \cdot 2.0\text{H}_2\text{O}$ structure as viewed along the a axis. Thermal ellipsoids are shown at the 50% probability level. Thermal ellipsoids with shaded segments are Na atoms. Small open circles are H atoms. The Na–O bonds are represented by dashed lines.

In $\text{Na}_{0.50}\text{VOPO}_4 \cdot 2.0\text{H}_2\text{O}$, each Na ion is octahedrally coordinated, though in a highly distorted fashion, with the coordination consisting of four water oxygens and two phosphate oxygens (Figure 3). The water molecules, $\text{H}_2\text{O}(11)$ and $\text{H}_2\text{O}(12)$, are coordinated to the V atoms. The other water molecules, $\text{H}_2\text{O}(13)$

and $\text{H}_2\text{O}(14)$, are weakly held by hydrogen bonding. The Na ion and all the water oxygens reside at general positions. Although the sodium and potassium compounds have similar layer stackings, the c axis of the former is 2 times as long as c in the latter, since the K ions and $\text{H}_2\text{O}(7)$ water molecules are at special positions. The size of the alkali-metal cation plays an important role in the arrangement of the metal cations and water molecules between the layers. The compound $\text{Na}_x\text{VOPO}_4 \cdot 2.0\text{H}_2\text{O}$ produced by intercalation with $\text{NaI}(\text{aq})$ has three different composition ranges, namely, $x < 0.2$ (range I), $0.2 < x < 0.32$ (range II), and $0.35 < x < 0.46$ (range III).¹² In range III, the samples are all two-phase mixtures of phase I and phase II. The compound from the hydrothermal synthesis has $x = 0.5$, which is the upper limit for phase I.

The layered mixed oxide hydrates $\text{A}_x\text{VOPO}_4 \cdot y\text{H}_2\text{O}$ were originally prepared by redox intercalation reactions of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with iodides in aqueous solution. The structural data for these compounds were derived from powder X-ray diffraction, and the lattice constants in the tetragonal and orthorhombic systems were reported. The phases reported herein crystallize in the triclinic space group $P\bar{1}$, although their alkali-metal and water contents are similar to those of the previous work. This study shows the detailed structural features of these interesting layered compounds. Since the hydrothermal method is a useful technique for growth of single crystals, the synthesis from cations in place of Na^+ or K^+ is currently under investigation.

Acknowledgment. Support for this study by the National Science Council and the Institute of Chemistry, Academia Sinica, is gratefully acknowledged.

Supplementary Material Available: Tables of crystal and refinement data, anisotropic thermal parameters, and bond angles and Figures S1 and S2, showing TG curves for both compounds and a view of the sodium compound along the b axis, respectively (7 pages); tables of observed and calculated structure factors for both compounds (16 pages). Ordering information is given on any current masthead page.

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Redetermination of the Crystal Structure of Hexaammincobalt(II) Chloride

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The crystal structure of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ has been redetermined at ambient and low temperatures. The compound forms cubic crystals, $a = 10.1342(7)$ Å at 294 K, with $Z = 4$. The structure has been refined in space group $Fm\bar{3}m$ with allowance for the rotationally disordered ammine ligands ($R = 0.025$, $R_w = 0.021$, 165 F_s [$>5\sigma(F)$]). The $\text{Co}^{\text{II}}\text{--N}$ bond length is 2.170(2) Å. Diffraction measurements at 128 K yielded similar but less precise results [$a = 10.012(4)$ Å; $\text{Co}^{\text{II}}\text{--N} = 2.164(4)$ Å].

Introduction

The hexaammincobalt(II/III) couple occupies a pivotal position in the development of our understanding of electron transfer among coordination compounds. The fact that electron transfer between $\text{Co}(\text{NH}_3)_6^{2+}$ and $\text{Co}(\text{NH}_3)_6^{3+}$ is unusually slow was cited during the discussion of a paper by Libby in 1952;¹ Libby responded that a slow electron self exchange rate would be explained if it were eventually found that the cobalt–ligand distances are appreciably different in the two oxidation states; and Libby's hypothesis appeared to receive immediate support when another speaker² cited $\text{Co}(\text{II})\text{--N}$ and $\text{Co}(\text{III})\text{--N}$ bond lengths of 2.5 and 1.9 Å, which had been derived by Stoll in 1926 from X-ray powder diffraction data.^{3,4} The subsequent measurements and inter-

pretation of the $\text{Co}(\text{NH}_3)_6^{2+/3+}$ self-exchange rate have been the subject of an authoritative review by Geselowitz and Taube.⁵ We restrict our present comments to the dimensional changes associated with the reaction.

During the early 1960's, standard texts continued to cite the lengths of $\text{Co}(\text{II})\text{--N}$ and $\text{Co}(\text{III})\text{--N}$ bonds as 2.5 and 1.9 Å, respectively. One contemporary author used slightly different values whose origin is not clear (2.4 and 2.05 Å),^{6,7} but there was no evidence to contradict the hypothesis that the difference between the bond lengths was substantial. In 1966, it became clear that the difference between the $\text{Co}(\text{II})\text{--N}$ and $\text{Co}(\text{III})\text{--N}$ bond

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Table I. Crystal Data for $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ at 294 and 128 K

	294 K	128 K
space group	$Fm\bar{3}m$	
a , Å	10.1342 (7)	10.012 (4)
V , Å ³	1040.80 (8)	1003.6 (5)
empirical formula	$\text{CoH}_{18}\text{N}_6\text{Cl}_2$	
f_w	232.02	
Z	4	
D_{calc} , g cm ⁻³	1.492	1.536
$\lambda(\text{Mo K}\alpha)$, Å	0.71069	
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	21.0	
max transm coeff	0.793	
min transm coeff	0.710	
R	0.025	0.023
R_w	0.021	0.023

lengths in the hexaammine complexes had been greatly overestimated. The bond lengths reported in a preliminary account of single-crystal structure analyses of hexaamminecobalt(II) chloride and hexaamminecobalt(III) iodide were 2.114 (9) Å for Co(II)-N and 1.96 (2) Å for Co(III)-N.⁸ Both analyses were based on Weissenberg photographic diffraction data. The value of the Co(III)-N bond length was subsequently refined to 1.936 (15) Å, resulting in a bond-length difference $\Delta d_{\text{Co(II)-Co(III)}} = 0.18$ Å.⁹

The details of the original structure analysis and refinement of hexaamminecobalt(II) chloride were never published, partly because there was a reasonable expectation that the use of counter methods would soon enable the accuracy and precision of the Co(II)-N bond-length determination to be improved. Subsequent attempts (repeated at intervals over an extended period) to record diffraction data of high quality were, however, frustrated by problems in producing crystal specimens of acceptable size, stability and mosaicity. In retrospect, it seems probable that the greater sensitivity of counter measurements revealed problems of crystal quality that had remained undetected (or had been compensated by the scaling and averaging procedures) in the original film data. The experiments now reported are the first in which neither the internal checks during data processing nor the behavior of the structure during refinement have created any suspicion of systematic errors related to the quality of the crystals.¹⁰

Experimental Section

Synthesis. A mixture of CoCl_2 (3.0 g) in ethanol (50 mL) was sonicated to effect dissolution and was then degassed with dry N_2 . To the solution was added a solution of NH_4Cl (15 M, 75 mL), which had been degassed with NH_3 . The mixture was heated until all precipitates dissolved and was then slowly cooled, yielding pink, octahedral, extremely air-sensitive crystals of hexaamminecobalt(II) chloride. Failure to carry out all operations in an NH_3 atmosphere resulted in the formation of blue tetraamminecobalt(II) impurities due to the loss of NH_3 or yellow hexaamminecobalt(III) impurities due to oxidation.

Crystallography. The crystals were coated with a thin layer of silicone grease and then a layer of cyanoacrylate glue and mounted on glass fibers. Crystals prepared in this way were stable in air for up to 7 days. Lattice parameters were determined by a least-squares fit to the positive and negative θ angles of 25 independent reflections in the range $18 \leq \theta \leq 26^\circ$, measured and refined on an Enraf-Nonius CAD4-F diffractometer fitted with a graphite monochromator. For low-temperature measurements the crystals were cooled by a stream of evaporated liquid N_2 . Two complete octants of data were recorded at ambient temperature, and one octant of data was recorded at 128 K. The crystallographic data are summarized in Table I. Data were reduced and Lorentz, polarization, absorption ($8 \times 8 \times 8$ sampling points),¹¹ and decomposition corrections

Table II. Merging R Values for the Possible Space Groups

space group	no. of unique reflns	R_{merge}	reflcs treated as equiv ^a
$F23$	536	0.035	hkl, klh, lhk
$F432$	281	0.035	$F23$ plus $k\bar{h}l, l\bar{h}k, \bar{h}lk$
$F\bar{4}3m$	364	0.034	$F23$ plus khl, lkh, hlk
$Fm\bar{3}$	305	0.036	$F23$ plus $\bar{h}kl, l\bar{h}k, k\bar{h}l$
$Fm\bar{3}m$	203	0.036	all of the above

^a 1800 $\pm h, +k, +l$ reflections were recorded.

Table III. Positional Parameters ($\times 10^4$) and Thermal Parameters ($\times 10^3$, Å²) for $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$, Model e^a

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}
Co	0	0	0	27 (1)	27 (1)	27 (1)
Cl	2500	2500	2500	42 (1)	42 (1)	42 (1)
N	0	0	2141 (2)	59 (1)	59 (1)	33 (1)
H1	615	615	2494	70		
H2	-225	-840	2494	70		
H3	-840	225	2494	70		

^a The model is defined in Figure 1.

(24% after 46 h at 294 K and 17% after 6 h at 128 K) were applied by using local programs SUSCAD and ABSORB.¹²

The systematic absences and lattice symmetry were consistent with the space groups $F23$, $Fm\bar{3}$, $F432$, $F\bar{4}3m$ and $Fm\bar{3}m$. For each of these space groups, the subsets of reflections that are equivalent and may be averaged to give the independent reflections are different. Given the multiple redundancies among the recorded data, it was possible to calculate a residual R_{merge} for each of the five space groups. The values of R_{merge} were effectively equal, despite the fact that the subsets and numbers of reflections contributing to the residuals were quite different (Table II). There was thus no reason to expect detectable deviations from centrosymmetry, and further consideration was restricted to the two centrosymmetric space groups $Fm\bar{3}$ and $Fm\bar{3}m$.

In both of these space groups the Co, Cl, and N atoms occupy special positions, the Co atom being at the origin. The N atom is constrained by symmetry to lie on the z axis; its only positional variable is the z coordinate, and this determines the Co-N bond length. The symmetry about the Co-N bond is mm or $4mm$, depending on whether the space group is $Fm\bar{3}$ or $Fm\bar{3}m$. Neither symmetry is compatible with the 3-fold symmetry of the NH_3 group. The hypothesis that the 72 H atoms in the unit cell occupy a combination of 24-fold and 48-fold positions can be dismissed, since all the possible combinations lead to unacceptable geometries for the NH_3 group. Consideration of all cubic, orthorhombic and monoclinic space groups shows that only a triclinic unit cell with $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$ would be compatible with ordered NH_3 ligands. It follows that, so long as the structure is treated as cubic, the H atoms cannot be ordered and the NH_3 ligand must be treated as rotationally disordered. A number of models (Figure 1) for the disorder were investigated (see Results, below).

Full-matrix least-squares refinement calculations were made with SHELX-76.¹³ Scattering factors and anomalous dispersion corrections for Co (Co^0 for Co^{II}) and Cl^- were taken from the ref 14. The scattering factors for N and H were those supplied in SHELX-76.¹³ The final atomic coordinates are listed in Table III. An ORTEP plot of the unit-cell is shown in Figure 2.¹⁵ The observed and calculated structure amplitudes and a list of additional experimental parameters relating to the data collection have been deposited.

Results

As mentioned above, neither of the space groups $Fm\bar{3}$ and $Fm\bar{3}m$ is compatible with the 3-fold symmetry of the NH_3 ligand. In order to investigate the implied rotational disorder without bias toward a particular model, the hydrogen atoms were initially omitted and only the positional and thermal parameters of the

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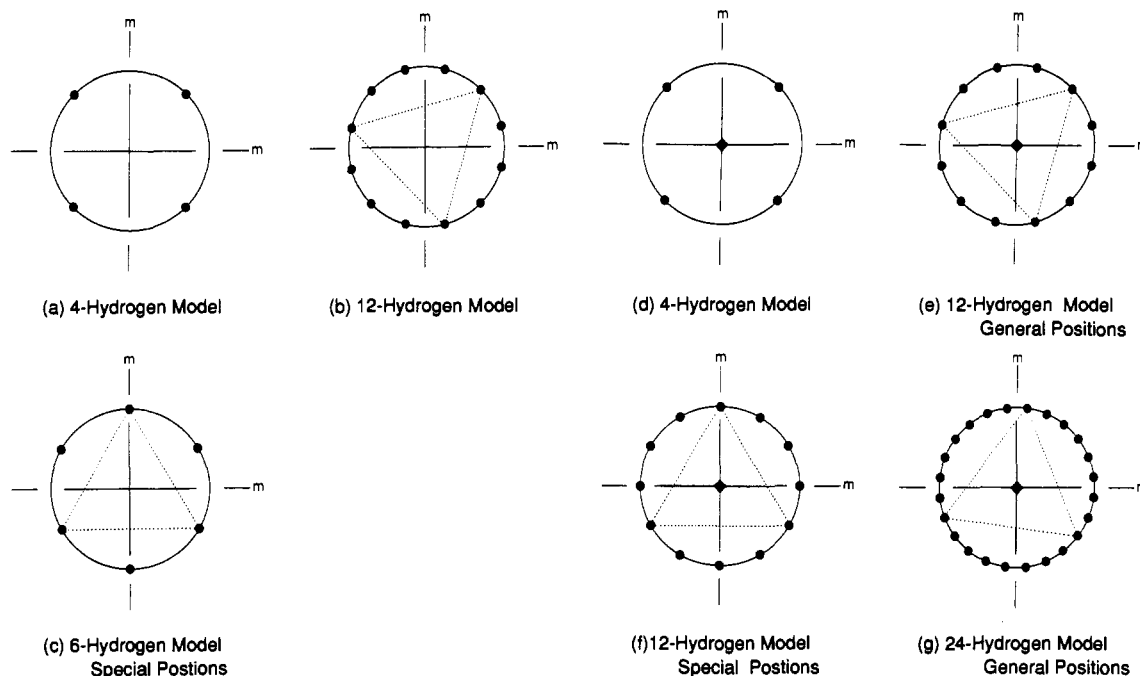


Figure 1. Diagrammatic representation of the models used to represent the H atom positions in the rotationally disordered NH_3 groups.

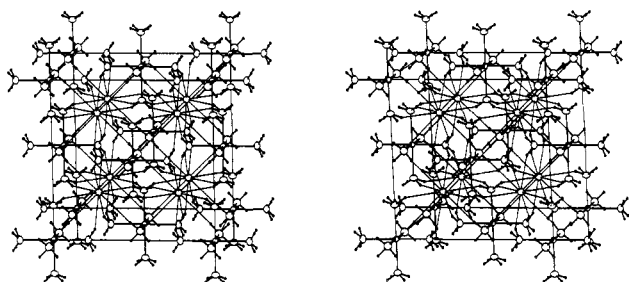


Figure 2. Stereoview¹⁵ of the unit cell of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$. The ammine groups are represented as an N plus four $3/4\text{H}$ atoms, the $3/4\text{H}$ atoms being shown in those positions of model e (Figure 1) that optimize N-H...Cl hydrogen bonding. Close contacts between H(ammine) atoms and chloride anions are shown as thin lines.

Co, N, and Cl atoms were refined to convergence. Two refinements were made in each space group, one with isotropic and the other with anisotropic thermal parameters for the N atom. Electron-density difference maps were then calculated. All the maps had only one significant feature, a peak with its maximum on the x, x, z plane and at 0.90 \AA from the N atom (Figure 1). The mm or $4mm$ symmetry transformed the peak into a quartet of peaks related by rotations of 90° about the Co-N bond.

In the simplest model for the observed residual electron-density, 0.75 H atom was placed at the position of each of the four electron-density difference peaks (Figure 1a,d). The obvious disadvantage of this model was its failure to represent any plausible disorder of the NH_3 group. A series of models were therefore generated by letting the mm or $4mm$ symmetry operate on an orientation of the NH_3 group, resulting in fractional H atom sites at equal intervals of $60, 30, \text{ or } 15^\circ$ on a circle centred on the x axis. The models had 6 or 12 H atom sites when special positions were occupied (Figure 1c,f), and 12 or 24 H atom sites when general positions were occupied (Figure 1b,e,g). While none of these models corresponded to an electron-density distribution with maxima at 90° intervals, two of them (b and e) had fractional H atoms on the $\pm x, \pm x, z$ planes, i.e., at positions close to the observed electron-density difference peaks.

In the refinement of models a-g, the NH_3 group was treated as a rigid body with N-H bond-lengths of 0.91 \AA , Co-N-H angles of 109.4° , and a fixed orientation. In models a and d, the ammine was treated as $\text{N}(3/4\text{H})_4$ with similar constraints. The results are summarized in Table IV. In a final refinement of the $4 \times$

Table IV. Details of Refinements for the Models Considered

space group	model ^a	no. of reflns ^b	no. of params	R	R_w	Co-N, \AA
$Fm\bar{3}$	a	238	8	0.025	0.023	2.171 (2)
	b		8	0.026	0.023	2.170 (2)
	c		8	0.026	0.023	2.170 (2)
$Fm\bar{3}m$	d	165	7	0.022	0.022	2.170 (2)
	e		7	0.025	0.021	2.170 (2)
	f		7	0.025	0.021	2.170 (2)
	g		7	0.029	0.027	2.171 (2)
	h ^c		11	0.021	0.015	2.167 (1)
$Fm\bar{3}m$ (128 K)	e		7	0.023	0.023	2.164 (2)

^aThe models are defined in Figure 1. ^b $I \geq 2.5\sigma(I)$. ^cModel h is a version of model d without the rigid-body constraints.

$3/4\text{H}$ atom model, the positional and thermal parameters of the H atom were treated as independent variables (Table IV, model h). The inclusion of anisotropic thermal parameters for the H atom did not result in a further decrease of the residual R . The N-H bond length at the end of the refinement of model h was $0.87 (1) \text{ \AA}$.

It is no matter of surprise that the lowest residuals R and R_w were obtained in the refinement with the largest number of variables (model h, $4 \times 3/4\text{H}$, unconstrained). Differences among the residuals for the other models were not sufficiently large to indicate that any model was to be preferred. The constrained model with the lowest residual R (model d) and the constrained models with the lowest residual R_w (models e and f) were refined in space group $Fm\bar{3}m$. All three had the same Co^{II}-N bond length, $2.170 (2) \text{ \AA}$. The difference between this value and the bond length in the unconstrained model, $2.167 (1) \text{ \AA}$, is not significant. As stated above, both model d ($4 \times 3/4\text{H}$, constrained) and model e ($12 \times 3/4\text{H}$ in general positions, constrained) had fractional H atoms near the maxima observed earlier in electron-density difference maps. The positions of these H atoms were appropriate for ammine...chloride hydrogen bonds [$\text{N} \cdots \text{Cl} = 3.601 \text{ \AA}$; $\text{H} \cdots \text{Cl} = 2.70 \text{ \AA}$].

The experiment at 128 K was originally undertaken to explore the possibility that $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$, by analogy with $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$,¹⁶ undergoes a phase change at low temperature. No persuasive evidence for a phase change at a temperature ≥ 128

K was found. Cooling the crystals resulted in a contraction of the lattice parameter by $\sim 1\%$, a broadening of the reflections by a factor of nearly 2, and an increase in the rate of crystal decomposition. Due to the higher mosaic spread of the crystals, the limit of resolution of the data was substantially lower than at ambient temperature. An electron-density difference map calculated after refinement of the non-H atom parameters was indistinguishable from the maps calculated using the room temperature data. Only model e was refined. The Co^{II}-N bond length was 2.164 (4) Å.

Discussion

The structure consists of Co atoms at the positions of a face-centered cubic lattice, Cl⁻ anions at all combinations of $\pm 1/4$, $\pm 1/4$, $\pm 1/4$, N atoms lying along the axes, and H atoms disordered on circles perpendicular to and centered on the axes (Figure 2). The NH₃ ligands make contacts with the Cl⁻ anions at distances which are consistent with weak hydrogen bonds. There are four symmetry-related Cl⁻ anions arranged around each NH₃ ligand, but in any orientation of the ligand only one H atom can be in the optimum position for forming a N-H...Cl bond. It is probable that the observed maxima in the H atom electron density at 90° intervals are a consequence of the H-bonding interactions. There are no significant nonbonded contacts within the lattice, the shortest Cl⁻...Cl⁻ distance being 5.07 Å.

The length of the Co^{II}-N bond in [Co(NH₃)₆]Cl₂ found in the present study, 2.170 (2) Å, is the most precise value reported to date. Similar bond-lengths occur in [Co^{II}(tacn)₂]I₂ (2.155 (15) Å),¹⁷ [Co^{II}(sepulchrate)](S₂O₈)₂ (average 2.164 (12) Å),¹⁷ [Co(NH₃)₆](PF₆)₂ (2.183 (2) Å),¹⁹ and [Co(NH₃)₆](BF₄)₂ (2.186

(10) Å).¹⁹ The significantly lower value in the complex of the macrocyclic ligand tacn²⁰ is due to steric constraints; both it and the unstrained value in the sepulchrate²⁰ complex are well reproduced by molecular-mechanics calculations.²¹ The structures of [Co(NH₃)₆](PF₆)₂ and [Co(NH₃)₆](BF₄)₂ were refined in the same space group as [Co(NH₃)₆]Cl₂, *Fm* $\bar{3}$ *m*.¹⁹ These salts differ from [Co(NH₃)₆]Cl₂ by having anions that do not form strong hydrogen bonds with NH₃. The infrared spectra are consistent with hydrogen bonding in [Co(NH₃)₆]Cl₂ but not in [Co(NH₃)₆](PF₆)₂ and [Co(NH₃)₆](BF₄)₂.¹⁹

In the time that has elapsed since the 1969 comparison between the Co-N bond lengths in [Co(NH₃)₆]Cl₂ and [Co(NH₃)₆]I₃,⁹ the structures of a number of other [Co(NH₃)₆]³⁺ salts have been reported. In most cases, the achievement of high precision was hampered by large unit cells, disorder, and/or high thermal motion. For example, 11 Co^{III}-N bond lengths ranging from 1.955 (9) to 1.983 (11) Å (with a mean of 1.966 Å) were derived from the structure of [Co(NH₃)₆]Cl₃ which crystallizes with an asymmetric unit of four formula units.²² The most precise published value for the Co^{III}-N bond length in a [Co(NH₃)₆]³⁺ salt is 1.965 (1) Å in [Co(NH₃)₆][FeCl₆].²³ We conclude that the current best estimate of the difference between the Co-N bond lengths in [Co^{II}(NH₃)₆]²⁺ and [Co^{III}(NH₃)₆]³⁺ is 0.205 (3) Å.

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Supplementary Material Available: Tables S2 and S3, listing additional crystal data specifications and positional and thermal parameters at 128 K (2 pages); Table S1, listing observed and calculated structure factors (1 page). Ordering information is given on any current masthead page.

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Bis(dioxolene)bis(pyridine)ruthenium Redox Series

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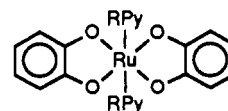
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A series of ruthenium complexes containing noninnocent 1,2-dioxolene ligands (dioxolene refers to any of the series catechol-semiquinone-quinone) have been prepared. These have the formula t -[Ru(RPy)₂(dioxolene)₂]^{*n*}, where the RPy ligands are a series of substituted pyridines and $n = -1, 0, +1$. Their electrochemical and spectroscopic (NMR, ESR, IR, PES, electronic) properties are reported and discussed in terms of their electronic structures, described by using simple qualitative molecular orbital models. Their electronic structures are subtly different from those of the related c -[Ru(bpy)(dioxolene)₂]^{*n*} species reported previously (bpy = 2,2'-bipyridine). The neutral ($n = 0$) complexes have a fully delocalized, mixed-valence Ru^{III}(RPy)₂(catechol)(semiquinone) electronic structure. The oxidized ($n = +1$) and reduced ($n = -1$) species are also Ru^{III} species. The electronic absorption data show a variety of different charge-transfer bands whose assignments are based upon energy variations with change of pyridine and/or dioxolene substituent and upon the net oxidation state.

Introduction

1,2-Dioxolenes, members of the catechol-semiquinone-quinone redox chain, have orbitals that are close in energy to the transition-metal d orbitals. The charge distribution in dioxolene coordination complexes depends upon the relative energies and overlap of these metal and dioxolene ligand orbitals.²³ In general,

Chart I



the energies are sufficiently disparate that the metal and dioxolene levels remain discrete within the electronic structures of these complexes. This is in sharp contrast to the closely related dithiolene ligands, which form complexes characterized by extensive

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