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Pressure Dependence of the Rate Constants for the Electron/Atom Self-Exchange between $M^{II}(cp)_2$ and $M^{IV}(cp)_2X^+$ (M = Ru, Os; X = Br, I) as a Function of Solvent

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The rate constants for the atom/electron self-exchange between $Ru(cp)_2$ and $Ru(cp)_2Br^+$ (cp represents the cyclopentadienide anion), $Ru(cp)_2$ and $Ru(cp)_2I^+$, and $Os(cp)_2$ and $Os(cp)_2I^+$ were measured by ^1H NMR line-broadening techniques as a function of pressure and solvent. The ranges of the volumes of activation as a function of solvent were from -2.3 ± 0.7 ($C_6D_5NO_2$) to -3.9 ± 0.5 cm^3/mol (CD_3NO_2) for the $Ru(cp)_2/Ru(cp)_2Br(PF_6)$ system, from -3.5 ± 1.0 (CD_3NO_2) to -7.7 ± 1.1 cm^3/mol (CD_3CN) for the $Ru(cp)_2/Ru(cp)_2I(CF_3SO_3)$ system, and from -7.6 ± 0.9 (CD_3CN) to 11.0 ± 1.0 cm^3/mol (($CD_3)_2CO$) for the $Os(cp)_2/Os(cp)_2I(CF_3SO_3)$ system. The $Os(cp)_2/Os(cp)_2I(CF_3SO_3)$ system was also studied for acetone/acetonitrile mixtures, and the volumes of activation were found to vary, in a nonlinear fashion, from -7.7 ± 0.9 to 15.9 ± 1.0 cm^3/mol. The enthalpy and entropy of activation were also measured for the mixed solvents and were found to be more like the acetone values than the acetonitrile values and were independent of mole fraction. The variation in ΔV^* and the occurrence of positive values are attributed to a significant contribution to the activation parameters from solvent displacement and a varying degree of solvation between the solvents investigated.

Introduction

The work presented here is an extension of our study of electron/atom self-exchange reactions between a metallocene, either $Ru(cp)_2$ or $Os(cp)_2$, and its halogenated M(IV) analog, $M(cp)_2Br^+$ or $M(cp)_2I^+$. Previous work has considered the effects of solvent, temperature, and concentration on the $Os(cp)_2/Os(cp)_2I^+$ reaction; additionally, solvent, temperature, concentration, and anion effects have been studied for the $Ru(cp)_2/Ru(cp)_2Br^+$ and $Ru(cp)_2/Ru(cp)_2I^+$ reactions, as well as the effect of pressure on the $Ru(cp)_2/Ru(cp)_2Br^+$ reaction with CD_3CN as the solvent.[1-3] The purpose of these studies is to provide a body of experimental data on a series of well-defined electron/atom self-exchange reactions in nonaqueous solvents and thus to test developing mechanistic concepts.[4] The $M(cp)_2/M(cp)_2X^+$ system is appealing for a broadly based and thorough study because the electron/atom self-exchange rate constants can be evaluated directly from ^1H NMR line broadening and because a series of complexes, with different metals, Ru and Os, different cyclopentadienides, cp and $(CH_3)_5(cp)$, different halogens, Cl, Br, and I, and different anions, PF_6, BF_4, and CF_3SO_3, can be synthesized. These complexes are substitution inert, somewhat soluble, and stable in a variety of solvents over a large temperature and pressure range.[5-7]

An interesting aspect of these reactions involves the possible mechanisms. The reaction could involve (a) X^+ transfer, (b) X transfer and a one-electron transfer in the reverse direction, or (c) X^- transfer and a two-electron transfer in the reverse direction. Each electron transfer could be an outer- or inner-sphere process which precedes or follows atom transfer. The two-electron process could be a concerted one or could involve one electron at a time. Also, more than one process could be occurring. For a thorough description of these mechanisms, see ref 4. Depending on the time scale, some of these mechanisms are indistinguishable; however, in a series of reactions in which M, X, solvent, and pressure are varied, a shift continuously or discontinuously toward one of the limiting mechanisms might occur. Since these reactions take place in solutions with no free halide and there is no apparent decomposition or loss of halide, we assume a halogen-bridged transition state. This has also been the assumption of Taube and co-workers.[5]

In this paper, we report kinetic investigations at various temperatures and pressures, up to 200 MPa, for the ruthenocene–iodoruthenocene (CD_3CN and CD_3NO_2), the ruthenocene–bromoruthenocene (CD_3CN, CD_3NO_2, and $C_6D_5NO_2$), and the osmocene–iodoosmocene (CD_3CN, CD_3NO_2, $(CD_3)_2CO$, $CDCl_3$ and $(CD_3)_2SO$) systems and for a series of mixed solvents between CD_3CN and $(CD_3)_2CO$.

Experimental Section

Ruthenocene was obtained from Strem Chemicals, Inc., and was purified by one vacuum sublimation. Osmocene was obtained from Strem Chemicals, Inc., and used without further purification. The M(IV) compounds were prepared as described previously.[2,5-7] The $M(cp)_2$ and $M(cp)_2X^+$ compounds were characterized by ^1H NMR spectroscopy and elemental analysis. All solvents used for purification were purchased from J. T. Baker Chemicals and purified by using standard procedures.[8] The deuterated solvents were purchased from MSD Isotopes, dried over 4-Å molecular sieves, and stored in the dark until used. In the kinetic experiments, the concentrations varied from 1 to 20 mM depending on solubility.

The pressure dependence data were collected on a Bruker WH-90 instrument. Acquisition parameters were a 1.5-μs pulse width, a 500-ms postacquisition delay, a 1000-Hz sweep width, a 4K block size, and 256-1000 pulses. To obtain accurate line widths, the field homogeneity was carefully adjusted for each spectrum on the basis of the amplitude of the ^2H lock signal. A nonspinning sample tube, similar to one described in the literature,[9] was used. It consisted of a 3.5-cm section taken from the bottom of a 5-mm NMR tube and extended with ca. 3 cm of heat-shrinkable Teflon tubing to transmit pressure. This tubing was plugged with a tapered glass rod.

Temperature was controlled with methanol circulating through a coiled path in the probe and a thermostated bath. The accuracy is ±1.0 K, and the precision is ±0.1 K. The temperature range was dictated by the freezing point of the particular solvent over the pressure range used and by the amount of line broadening observed at high pressures. The solvents were chosen on the basis of the stability and solubility of the $M(cp)_2$ complexes and varying dielectric constant.

The digitized data from the NMR spectrometer were transferred to a personal computer based on an 80286 processor. The rate analysis program used in this study employs equations derived from the Bloch equations[10,11] for exchange between two sites with nonequal populations

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Table I. Activation Volumes for the $Os(cp)_2/Os(cp)_2I(CF_3SO_3)$ Reaction as a Function of Solvent[a]

solvent	no. of pts	P, MPa	$\Delta V^{\ddagger}$, cm³/mol	T, K
CD_3CN	19	0.1–200	−7.6 ± 0.9	283
CD_3NO_2	14	0.1–200	−4.7 ± 1.0	268
$(CD_3)_2CO$	13	0.1–150	9.7 ± 0.8	283
$(CD_3)_2CO$	7	0.1–150	11.0 ± 1.0	293
$CDCl_3$	16	0.1–170	−2.7 ± 0.7	293
$CDCl_3$	11	0.1–170	−7.0 ± 0.8	303
$CDCl_3$	12	0.1–170	−5.0 ± 1.0	314
$(CD_3)_2SO$	22	0.1–170	0.07 ± 0.2	315

[a] Os(II) concentration ca. 10^{-3} M; see supplementary material. [b] Os(IV) concentration ca. 10^{-3} M; see text and supplementary material.

Table II. Activation Volumes for the $Ru(cp)_2/Ru(cp)_2I(CF_3SO_3)$ Reaction as a Function of Solvent[a]

solvent	no. of pts	$\Delta V^{\ddagger}$, cm³/mol	T, K
CD_3CN	11	−7.7 ± 1.1	271
CD_3CN	12	−4.8 ± 1.0	259
CD_3NO_2	11	−4.0 ± 0.9	278
CD_3NO_2	12	−3.5 ± 1.0	281

[a] Ru(II) concentration ca. 10^{-3} M; see supplementary material. [b] Ru(IV) concentration ca. 10^{-3} M; see text and supplementary material. Pressure 0.1–200 MPa.

Table III. Activation Volumes for the $Ru(cp)_2/Ru(cp)_2Br(PF_6)$ Reaction as a Function of Solvent[a]

solvent	no. of pts	P, MPa	$\Delta V^{\ddagger}$, cm³/mol	T, K
CD_3CN	10	0.1–200	−2.9 ± 0.1	306
CD_3CN	8	0.1–200	−2.7 ± 0.4	314
CD_3CN	9	0.1–200	−2.9 ± 0.1	315
CD_3CN	9	0.1–200	−3.1 ± 0.2	317
CD_3CN	11	0.1–200	−3.3 ± 0.2	328
$C_6D_5NO_2$	9	0.1–200	−2.3 ± 0.7	307
$C_6D_5NO_2$	9	0.1–200	−3.1 ± 0.6	306
$C_6D_5NO_2$	7	0.1–150	−2.8 ± 0.4	313
CD_3NO_2	9	0.1–200	−3.9 ± 0.5	315

[a] Ru(II) concentration ca. 10^{-3} M; see supplementary material. [b] Ru(IV) concentration ca. 10^{-3} M; see text and supplementary material.

and widths, including multiple pairs of lines, assuming no saturation and steady-state conditions. The NMR data analysis and the proton NMR spectra of each compound studied here have been described previously.[1–3]

From transition-state theory, the volume of activation is defined by $[\partial(\ln k)/\partial P]_T = -\Delta V^{\ddagger}/RT$. The volumes of activation were determined from analysis of ln k versus pressure plots. For a typical analysis, 7–22 data points were collected over a range of 0.1–200 MPa. A linear model was adequate to describe the data. The errors given for the volumes of activation were calculated from the scatter about the fit line. Overall errors are estimated to be about 2 times greater than these.

Results

Table I presents the activation volumes for the $Os(cp)_2/Os(cp)_2I(CF_3SO_3)$ reaction in five solvents. Two solvents, acetone and chloroform, were studied at several temperatures. Table II presents the volumes of activation for acetonitrile and nitromethane, each at two temperatures for the $Ru(cp)_2/Ru(cp)_2I(CF_3SO_3)$ reaction. Table III reports the activation volumes as a function of temperature and solvent for the $Ru(cp)_2/Ru(cp)_2Br(PF_6)$ reaction. The results of temperature and pressure dependencies for the $Os(cp)_2/Os(cp)_2I(CF_3SO_3)$ reaction in $CD_3CN/(CD_3)_2CO$ mixtures are given in Table IV.

Discussion

General patterns previously observed indicate that the iodine system reacts 2–3 orders of magnitude faster than the bromine system. These previous results are summarized in Table V. This is generally attributed to the formation of a more stable precursor complex with iodine as the bridging atom and better electron

Table IV. Enthalpy, Entropy, Volume of Activation, and Rate Constant at 20 °C as Functions of Mixed Solvent for the $Os(cp)_2/[Os(cp)_2I](CF_3SO_3)$ Reaction[a]

solvent[b] mole fraction	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol K)	$\Delta V^{\ddagger}$, cm³/mol	k_{12}, M⁻¹ s⁻¹
1.0	11.3 ± 0.2	2.5 ± 0.2	10.5 ± 1.0	78.3 × 10³
0.87	9.3 ± 0.2	−2.0 ± 0.5	15.5 ± 1.0	2.57 × 10⁵
0.58	9.4 ± 0.2	−1.9 ± 0.5	14.7 ± 1.0	2.28 × 10⁵
0.08	11.5 ± 0.2	5.0 ± 0.5	15.4 ± 1.0	1.99 × 10⁵
0.0	7.6 ± 0.1	−13.3 ± 0.3	−7.6 ± 0.9	17.6 × 10³

[a] Os(II) concentration 10^{-3} M; see text and supplementary material. Os(IV) concentration 10^{-3} M; see text and supplementary material. Temperature range 268–313 K; see supplementary material. Pressure range 0.01–170 MPa; see supplementary material. Number of pressure points 11–22. [b] Mole fraction of $(CD_3)_2CO$ in $(CD_3)_2CO/CD_3CN$ mixtures.

mediation by iodine. Neither series, ruthenium or osmium, was sensitive to the identity of the anion, but the iodine system was somewhat more sensitive to the nature of the solvent. For the $Ru(cp)_2/Ru(cp)_2Br(PF_6)$ reaction, three solvents, nitromethane, acetonitrile, and nitrobenzene, were studied here as a function of pressure. The temperature dependence of the reaction has been previously reported, and the entropies of activation were found not to vary much with solvent (−14.1 to −15.7 cal/(mol K)).[2] As with the other activation parameters, the volumes of activation for the $Ru(cp)_2/Ru(cp)_2Br$ system were found to be insensitive to the solvents studied, varying only from −2.3 to −3.9 cm³/mol. The temperature dependence of the volume of activation was also studied in nitrobenzene and acetonitrile and within the limited range investigated was found to be independent of temperature.

In previous studies, the $Ru(cp)_2/Ru(cp)_2I^+$ rate constant displayed significant variation with solvent.[2] Another notable difference was found for nitromethane, which had higher enthalpy and entropy of activation compared to acetonitrile. In order to better interpret these results, volumes of activation were measured in these same two solvents. If the average of the two temperatures is taken, then the volume of activation for acetonitrile is −6.2 cm³/mol and that for nitromethane is −3.7 cm³/mol; see Table II. This is not a dramatic difference in view of the large, 8 cal/(mol K), difference in the entropy of activation between the solvents. The most positive entropy of activation, −0.5 cal/(mol K), and the most positive volume of activation, −3.7 cm³/mol, are for nitromethane. Unfortunately the $Ru(cp)_2I^+$ ion is unstable in acetone; thus the comparison between Ru and Os reactions cannot be made for that solvent.

The $Os(cp)_2/Os(cp)_2I^+$ reaction was found to be very solvent sensitive in the previous temperature dependence studies.[3] The volumes of activation reported here vary from +10.5 to −7.6 cm³/mol, displaying the largest solvent effects of the series studied. Five solvents were studied (see Table I); other solvents which had been previously studied could not be studied here due to either limited solubility or the magnitude of rate constants that could be measured on the lower field instrument used for the high-pressure experiments. Three solvents, chloroform, nitromethane, and acetonitrile, showed negative $\Delta V^{\ddagger}$ while dimethyl sulfoxide and acetone gave positive values. If the low dielectric constant solvent, chloroform, is not considered, then there is a good linear correlation between entropy and volume of activation. Other studies of the solvent dependence of the volume of activation have shown only moderate effects. For instance, the hexakis(cyclohexyl isocyanide)manganese(I,II) electron self-exchange system was measured in eight solvents and the $\Delta V^{\ddagger}$ was always negative, only varying by 10 cm³/mol.[12] Tris(hexafluoroacetylacetonato)ruthenium(II,III) electron self-exchange volumes of activation were found to only vary 3.5 cm³/mol in four different solvents.[13] These reactions are outer-sphere electron transfer and not directly comparable to the atom/electron transfer reactions.

The variation of $\Delta V^{\ddagger}$ does not correlate directly with solvent parameters such as molar volume, viscosity, dielectric constant

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Table V. Activation Parameters and Observed Second-Order Rate Constants at 20 °C in Various Solvents

solvent (ϵ)	no. of pts	T range, ± 1 °C	ΔH^*, kcal/mol^{-1}	ΔS^*, cal mol^{-1} K^{-1}	$10^{-3}k$,[a] M^{-1} s^{-1}
		Os(cp)$_2$/[Os(cp)$_2$I]CF$_3$SO$_3$			
(CD$_3$)$_2$SO (46.7)	18	+20 to +60	12.6 $\pm$ 0.2	0.0 $\pm$ 0.7	3.5
(CD$_3$)$_2$CO (20.7)	14	−20 to +40	11.3 $\pm$ 0.2	2.5 $\pm$ 0.6	78.3
CD$_3$CN (37.5)	16	−20 to +70	7.5 $\pm$ 0.1	−13.4 $\pm$ 0.4	17.6
CD$_3$NO$_2$ (35.8)	5	−10 to +40	7.0 $\pm$ 0.2	−13.9 $\pm$ 0.6	31.3
CDCl$_3$ (4.7)	24	−30 to +55	4.8 $\pm$ 0.1	−27.1 $\pm$ 0.3	2.0
		Ru(cp)$_2$/[Ru(cp)$_2$I]CF$_3$SO$_3$			
CD$_3$CN	17	−30 to +20	6.7 $\pm$ 0.2	−8.7 $\pm$ 0.8	7.4[b]
CD$_3$NO$_2$	14	−10 to +35	8.5 $\pm$ 0.3	−0.5 $\pm$ 0.7	19.2[b]
		Ru(cp)$_2$/[Ru(cp)$_2$Br]PF$_6$			
CD$_3$CN	6	+20 to +70	8.2 $\pm$ 0.1	−15.7 $\pm$ 0.3	1.6[c]
CD$_3$NO$_2$	5	+20 to +60	8.5 $\pm$ 0.1	−14.1 $\pm$ 0.5	2.5[c]
C$_6$D$_5$NO$_2$ (34.8)	16	+20 to +110	8.1 $\pm$ 0.1	−14.8 $\pm$ 0.2	2.9[c]

[a] Apparent second-order rate constants. [b] In the slow-exchange regime, the rate constants were determined by using the broadenings of both the Ru(II) and Ru(IV) signals; an average rate constant is given. [c] Concentration range of [Ru(cp)$_2$Br]PF$_6$: 9.9–19.1 mM.

(ϵ), density (d), specific conductance, dipole moment, or donor number (DN). There is a tenuous correlation with four of the solvents with the index of refraction. With increasing index of refraction, the volume of activation becomes more positive; however, acetone does not show a correlation. In fact, acetone has one of the smallest indices of refraction and yet has the most positive ΔV^*. There is a rough correlation between molar polarizability [($\epsilon - 1$)/($\epsilon + 2$)](M/d) and ΔV^*. The larger the polarizability of the solvent, the more positive the volume of activation.

There is also a rough correlation between the volumes of activation and acceptor numbers. In general, the smaller the acceptor number, the more positive the ΔV^*. In previous attempts to correlate ΔH^* and ΔS^* with donor/acceptor numbers, no trend was found. This was explained in view of the fact that donor/acceptor numbers are developed for hard–hard interactions and therefore would not apply to the soft reaction center in the Os-(cp)I$^+$ system. The rough correlation seen here may be just coincidental, but it also may suggest that solvation of the I atom acting as a Lewis base is influential.

The lack of any direct correlation with bulk solvent parameters is probably due to several factors. One is that the pressure dependence of these terms is actually what should be used; however, such data are extremely limited or completely unavailable. Secondly, the empirical numbers for solvents are for hard–hard Lewis-type interactions such as donor numbers and should not be appropriate for these soft reactant centers, such as I and aromatic ring systems. Another complication arises when high versus low dielectric constant solvents are compared because, in the low dielectric constant solvents, ion pairs are presumably present. Also, in low dielectric constant solvents, and at M(IV) concentrations below 4 mM, these reactions were found to follow a rate law zero order in M(IV) and first order in M(II). In the present study, the M(VI) concentration was kept at or above 4 mM, where it has been shown that the bimolecular path will be dominant and direct comparison to the results for the higher dielectric constant solvents is justified.[2,3]

If the trends in the activation parameters are taken as primarily arising from the solvent reorganization and displacement required to form a bridged transition state, then the pattern observed can be rationalized as follows. The interaction between the M(cp)$_2$ center and the halogen to form the precursor complex should have a negative contribution to ΔH^*, ΔS^*, and ΔV^*. However, to the extent that solvent must be displaced to allow the bridging geometry to be attained and since there is a decrease in charge density when a neutral and a +1 reactant form a +1 complex, there should be a positive contribution to each of the activation parameters. The more strongly solvated the reactants, the larger will be the contribution from solvent release.

The differences between the solvents can be qualitatively explained in the following manner. If the precursor complex formation is dominating the observed parameters, then the difference

between the solvents is due to the interactions of the complexes with the solvent and subsequent displacement of solvent. In solvents that are better at solvating the reactants, one would expect positive ΔH^*, positive ΔS^*, and positive ΔV^*, relatively. In low dielectric constant solvents, ion pairs will be present, and these will be solvated less than the fully charged species. In solvents that are poor at solvating the reactants, or in low dielectric constant solvents where ion pairs will be less solvated, one would expect smaller, less positive ΔH^*, more negative ΔS^*, and smaller or more negative ΔV^*. These trends are observed in the experimental data for all three reaction series studied here. The dominant factor is solvent release in the formation of the precursor complex. Reducing the charge by forming ion pairs decreases solvation and diminishes the effect. Solvents containing an oxygen atom appear to strongly solvate the reactants.

Because of our desire to better understand the molecular details of solvent reorganization in these systems and because of our interest in solvation, the activation parameters for the Os system were studied in a mixed solvent. Acetone and acetonitrile were chosen for the mixed-solvent study because they are miscible and their activation parameters are much different. The activation parameters for the mixed solvents are nearly the same as those for the pure acetone values; see Table IV. Even at a 0.08 mole fraction of acetone, all three activation parameters resemble the acetone values rather than the acetonitrile values. The fact that the shift in activation parameters occurs with relatively small amounts of acetone is indicative of substantial preferential solvation. The experimental data follow the argument given above because one would expect that the solvent which is better at solvating the reactants would solvate them and then would be released on the formation of the precursor complex. The nonlinear trends may be due to the precision of the measurements; however, nonlinear behavior has been observed before. In a series of asymmetric bridged systems, (2,2-bipyridine)$_2$ClRu–L–Ru-(NH$_3$)$_4$(pyridine)$^{+5/+4/+3}$, non-linear trends in ΔH_{app} and ΔS_{app} for the intervalence electron transfer were observed as a function of solvent composition in mixtures of DMSO and acetonitrile.[14,15] In these systems, an asymmetric "spike" was observed in about the 99–95% mole fraction range. Preferential solvation was used to explain the experimental data.

Conclusion

Overall, the observed data follow the arguments given above in that the dominant factor controlling the activation parameters appears to be the solvation of the reactants which must be lost on going to the transition state. Within these proposed models, it has been assumed that there is a bridged transition state. In

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low dielectric constant solvents, ion pairing reduces the strength of solvation and the counterion displaces solvent, thus decreasing the solvent contribution. The variation in the solvent contribution can apparently overcome other contributions and even change the sign of $\Delta V^{\ast}$.

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Compounds Containing Linked, Multiply-Bonded Dimetal Units. 1. Tetrakis(μ-6-chloro-2-hydroxypyridinato)diruthenium(II,III) Cations Linked Axially by Pyrazine. Comparison with a Single Molecule Axially Coordinated by Pyridine

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The tetranuclear compound [{Ru$_2$(chp)$_4$}$_2$(pyz)](BF$_4$)$_2$ and the dinuclear compound [Ru$_2$(chp)$_4$(py)](BF$_4$) were prepared by substitution of an axial chloride ligand of Ru$_2$(chp)$_4$Cl with pyrazine and pyridine, respectively. Each compound has been characterized by X-ray crystallography and by magnetic susceptibility measurements from ca. 5 to ca. 300 K. [{Ru$_2$(chp)$_4$}$_2$-(pyz)](BF$_4$)$_2$ crystallizes with four solvent molecules in space group $P2_1/c$ (No. 14). With (CH$_2$Cl$_2$)$_2$ and (pyz)$_2$ the unit cell has $a = 12.414$ (3) Å, $b = 16.083$ (5) Å, $c = 17.812$ (4) Å, $\beta = 97.915$ (2)°, $V = 3522$ (2) Å, and $Z = 2$. With (CH$_2$Cl$_2$)$_4$, the very similar unit cell has $a = 12.081$ (4) Å, $b = 16.469$ (4) Å, $c = 17.209$ (3) Å, $\beta = 98.28$ (2)°, $V = 3390$ (2) Å^3, and $Z = 2$. [Ru$_2$(chp)$_4$(py)](BF$_4$) crystallizes in a triclinic cell with $a = 13.907$ (3) Å, $b = 16.322$ (3) Å, $c = 9.168$ (1) Å, $\alpha = 106.09$ (1)°, $\beta = 99.89$ (2)°, $\gamma = 76.88$ (2)°, $V = 1934$ (1) Å^3, and $Z = 2$. The pyrazine ligand bridges two diruthenium species in the [{Ru$_2$(chp)$_4$}$_2$(pyz)]$^{2+}$ cation, and the pyridine ligand coordinates to one axial position in the [Ru$_2$(chp)$_4$(py)]$^+$ ion. The pyridine or pyrazine nitrogen atoms are in all cases attached to the ruthenium atoms that are coordinated by oxygen atoms. The two complexes show similar magnetic behavior; they exhibit Curie–Weiss behavior, and the decrease in moment at low temperatures results primarily from zero-field splitting effects. There is no significant magnetic exchange interaction between the two dinuclear species in the [{Ru$_2$(chp)$_4$}$_2$(pyz)]$^{2+}$ ion.

Introduction

The work to be reported in the series of papers of which this is the first lies at the intersection of two lines of study. The electronic interactions, especially magnetic interactions, between paramagnetic transition metal atoms linked by bridging groups is an old and heavily explored field[1] although still full of challenging problems. On the other hand there has recently been emerging a new research thrust concerning the synthesis of oligomers and polymers that consists of multiply-bonded dimetal units linked together, in various ways, by shared bi- and multidentate ligands.[2]

The dinuclear multiply-bonded compounds of ruthenium and osmium have been extensively investigated in this laboratory in recent years, and we have been able to clarify their electronic structures quite considerably. The main species are built on Ru$_2$$^{4+}$, Ru$_2$$^{5+}$, and Os$_2$$^{6+}$ cores, all of which display full or partial paramagnetism. Moreover, this paramagnetism arises, in whole or in part, from the presence of unpaired electrons in M–M π^* orbitals. It should therefore be possible, at least in principle, to build interactive pathways between such M$_2$ cores by connecting them, through their axial positions, by bridging ligands that have π systems of their own. That, in summary, is the concept that we shall be trying to implement in the work to be reported in this series of papers.

We begin here with very simple questions: (1) If we take two molecules that contain Ru$_2$$^{5+}$ cores in their quartet ground states based on the $\sigma^2\pi^4\delta^2\pi^{*2}\delta^*$ configuration, can we couple them by some bidentate ligand that has a π system? (2) If we do so, will there be a detectable magnetic coupling of some kind between the linked Ru$_2$$^{5+}$ cores?

In our first effort to address these questions we have chosen the tetrakis(μ-6-chloro-2-hydroxypyridinato)diruthenium(II,III)

cation[3] (as its BF$_4$$^-$ salt) and employed pyrazine, 1,4-diazabenzene, as the linking ligand, since this molecule has previously been used successfully in other systems.[4–9] To have a standard for the behavior of an individual molecule with as similar a set of ligands as possible, we have also prepared and studied the same Ru$_2$$^{5+}$ complex containing pyridine as the axial ligand.

Experimental Section

The starting material, Ru$_2$(chp)$_4$Cl, was prepared by using a literature procedure.[3] Ag(CH$_3$CN)$_4$BF$_4$ was prepared by addition of acetonitrile to AgBF$_4$.

Preparation of [{Ru$_2$(chp)$_4$}$_2$(pyz)](BF$_4$)$_2$ (1). A 0.25-g (0.33-mmol) sample of Ru$_2$(chp)$_4$Cl and 0.21 g (0.66 mmol) of Ag(CH$_3$CN)$_4$BF$_4$ were dissolved in 20 mL of dichloromethane and stirred overnight under argon. A white precipitate of AgCl and some unreacted AgBF$_4$ were removed by filtration. Evaporation of the filtrate provided [Ru$_2$(chp)$_4$-(CH$_3$CN)](BF$_4$), which is very hygroscopic. This intermediate was dissolved in 20 mL of CH$_2$Cl$_2$, and pyrazine, 0.053 g (0.66 mmol), was added. This solution was heated to reflux for 2 h and cooled, and hexane was added to precipitate a dark purple solid. Yields were typically 0.25–0.30 g (ca. 50%). IR (KBr, cm^{-1}): 3100 w, 1594 s, 1527 s, 1437 s, 1388 m, 1339 s, 1225 w, 1172 s, 1054 s, 1015 s, 934 m, 876 s, 792 s, 722 s, 630 s. Crystalline material suitable for X-ray work and magnetic study was obtained by slow diffusion of hexane into a portion of the CH$_2$Cl$_2$ solution. The solvent content of the crystals varies, in a way which we do not understand. In one case we obtained 1·4CH$_2$Cl$_2$. For further details see below under X-ray crystallography.

Preparation of [Ru$_2$(chp)$_4$(py)](BF$_4$)·hexane·py (2). A 50-mL volume of pyridine was added to [Ru$_2$(chp)$_4$(CH$_3$CN)](BF$_4$) instead of pyrazine in a similar procedure, and the reaction mixture was stirred overnight.

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