that there is little, if any, assistance by the entering group on the activated complex for substitution.[32]

Acknowledgment. Support of this work by National Institutes of Health Grant No. GM13638-16 is gratefully acknowledged.

Registry No. $[(NH_3)_4RuNH_2CH_2CONCH_2COOH][Cr(NH_3)_2(SCN)_4]_2$, 85320-34-9; $[(NH_3)_4RuNH_2CH_2CONH](PF_6)_2$, 85320-36-1; $[(NH_3)_4RuNH_2CH_2CONCH_2CH_3](PF_6)_2$, 85320-38-3; $[(NH_3)_4RuNH_2CH_2CONH_2](PF_6)_2$, 85320-40-7; $[(NH_3)_4RuNH_2CH_2CONHCH_2CH_3](PF_6)_2$, 85320-42-9; $[(NH_3)_4RuNH_2CH_2CONHCH_2COOH][Cr(NH_3)_2(SCN)_4]_2$, 85335-31-5; $[(NH_3)_4RuNH_2CH_2COO](PF_6)_2$, 85335-32-6; $[(NH_3)_4RuNH_2CH_2COO]^{2+}$, 85320-43-0; $[(NH_3)_4RuNH_2CH_2CONH]^{2+}$, 85320-35-0; $[(NH_3)_4RuNH_2CH_2CONCH_2CH_3]^{2+}$, 85320-37-2; $[(NH_3)_4RuNH_2CH_2CONCH_2COOH]^{2+}$, 85320-44-1; $[(NH_3)_4RuNH_2CH_2CONCH_2COO]^{+}$, 85320-33-8; $[(NH_3)_4RuNH_2CH_2CONH_2]^{3+}$, 85320-45-2; $[(NH_3)_4RuNH_2CH_2CONHCH_2CH_3]^{3+}$, 85320-46-3; $[(NH_3)_4RuNH_2CH_2CONHCH_2COOH]^{3+}$, 85335-33-7; $[(NH_3)_4RuNH_2CH_2CONHCH_2COO]^{2+}$, 85320-47-4; $[(NH_3)_4RuNH_2CH_2COO]^{+}$, 85320-48-5; $[(NH_3)_4RuNH_2CH_2CONH_2]^{2+}$, 85320-39-4; $[(NH_3)_4RuNH_2CH_2CONHCH_2CH_3]^{2+}$, 85320-41-8; $[(NH_3)_4RuNH_2CH_2CONHCH_2COOH]^{2+}$, 85320-49-6; $[(NH_3)_5Ru^{III}NHCOCH_3]^{2+}$, 52843-03-5; $[(NH_3)_5Ru^{III}NHCOC_6H_5]^{2+}$, 52843-05-7; $[(NH_3)_5Ru^{III}NH_2COC_6H_5]^{3+}$, 52843-10-4; 4-CNpy, 100-48-1; bis(4-cyanopyridine)tetraammineruthenium(II), 85320-50-9; *cis*-tetraamminediaquoruthenium(III) trifluoromethanesulfonate, 74468-24-9; acetonitrile, 75-05-8.

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Contribution from the Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

Structural and Mechanistic Studies of Coordination Compounds. 35. Steric Effects and the Dissociative Mechanisms for Simple Ligand Substitution Reactions and Base Hydrolysis of Some Ruthenium(III) Amine Complexes

CHUNG-KWONG POON* and TAI-CHU LAU

Received June 28, 1982

Kinetics of substitution reactions of *trans*-$[Ru(teta)Cl_2]^+$ by bromide and of *trans*-$[Ru(L)Br_2]^+$ (L = teta or tetb) by chloride have been studied over a range of temperatures. The observed steric acceleration of k_1(tetb) > k_1(teta) > k_1(cyclam) for the release of the first coordinated halide from analogous dihalogen complexes supports a dissociative mechanism for these reactions. A similar trend of steric acceleration has also been found to support the S_N1cB mechanism for the base hydrolysis of *trans*-$[Ru(L)ACl]^+$ (L = tetb, teta, or cyclam; A = Cl or OH).

Introduction

Ligand substitution reactions of ruthenium(III) amine complexes have received much attention in recent years.[1-11] Conflicting arguments have been advanced to support either a dissociative or an associative mechanism under different experimental conditions. The first systematic study[2] on the *cis*-tetraammineruthenium(III) series of complexes showed that charge had little effect on the aquation rates, and an associative mechanism was invoked. However, Ohyoshi et al.[5] have demonstrated the existence of a linear free energy relationship with unit slope, though over only one logarithmic unit, for the aquation of $[Ru(NH_3)_5X]^{2+}$ complexes (X = some halogen-substituted carboxylate ligands). This indicated a dissociative mechanism. A dissociative mechanism was also supported by the aquation study of $[Ru(NH_3)_5Cl]^{2+}$ and *cis*-$[Ru(en)_2Cl_2]^+$ in a variety of water–organic solvent mixtures[7] and by the observation[9] that the aquation rates of *trans*-$[Ru(L)Cl_2]^+$ decreased with increasing chelation of L: $(NH_3)_4 \approx (en)_2$ > (*R*,*S*)-2,3,2-tet > cyclam, where en, 2,3,2-tet, and cyclam represent ethylenediamine, 3,7-diazanonane-1,9-diamine and 1,4,8,11-tetraazacyclotetradecane, respectively. Recently, Fairhurst and Swaddle[11] have examined the effect of pressure on both the forward aquation and the reverse anation of $[Ru(NH_3)_5Cl]^{2+}$. The observed negative volumes of activation for both processes were taken to support an associative mechanism. The aim of this investigation is to examine the steric effects on rates in order to resolve this mechanistic ambiguity.

The structure of *trans*-$[Ru(teta)X_2]^+$ (X = Cl or Br) is known from the crystallographic work[12] on *trans*-$[Ru(teta)Br_2]_2[ZnBr_4]$ to possess the same skeleton as *trans*-$[Ru(cyclam)Cl_2]^+$ (structure I),[13] where teta represents *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. The structure of *trans*-$[Ru(tetb)X_2]^+$ (X = Cl or Br) is not known, where tetb is the racemic isomer of teta. However, it is most likely that these tetb complexes possess structure II by reference to that of $[Ni(tetb)]^{2+}$,[14] in which the steric environments above and below the RuN_4 plane are different. The studies of the relative rates of release of these halide ions from corresponding tetb, teta, and cyclam complexes would yield important information about the influence of steric effects on ruthenium(III) substitution reactions. Work has also been extended to investigate steric effects on the base hydrolysis

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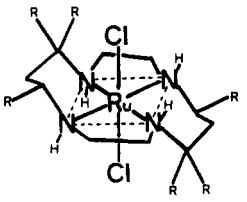
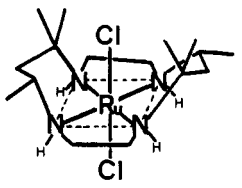


I

R = H, cyclam complex
R = CH_3, teta complex



II

of these systems in order to test the proposed S_N1cB mechanism.[1,3,10]

Experimental Section

Complexes *trans*-$[Ru(L)X_2]ClO_4$[15] (L = teta or tetb, X = Cl or Br) and *trans*-$[Ru(cyclam)X_2]X$[16] (X = Cl or Br) were prepared according to published methods.

Kinetics. Halide substitutions were followed spectrophotometrically either in situ or by the sealed-tube method with a Unicam SP8000 recording spectrophotometer equipped with a Weyfringe ADCP-2 digital-printer accessory. Base hydrolysis was followed in situ with an Aminco-Morrow stopped-flow spectrophotometer equipped with an Aminco-DASAR (data acquisition, storage, and retrieval) system. Experimental details on data collection, temperature control, and data treatment have been described previously.[17]

Results

(1) Kinetics of Halide Substitution Reactions of *trans*-$[Ru(L)X_2]^+$ (L = teta or tetb; X = Cl or Br). Preliminary studies showed that *trans*-$[Ru(L)X_2]^+$ easily underwent dehydrogenation reactions in dilute acids, even in degassed solutions. However, dehydrogenation was efficiently quenched by excess acids and halides (>1 M in each case). Hence, halide substitution reactions rather than simple aquation were investigated for these systems. Since it has been shown[18] that the rates of substitution for the first coordinated chloride in *trans*-$[Ru(en)_2Cl_2]^+$ are independent of the nature and concentrations of the incoming nucleophiles and are equal to the aquation rate, it is reasonable to assume that the halide substitution reactions studied here, which are independent of the concentrations of the incoming halide (see later), would give an alternative measure of the aquation rates according to reactions 1 and 2, where X^- and Y^- are two different halides.

$$trans\text{-}[Ru(L)X_2]^+ + H_2O \xrightarrow{\text{slow}} trans\text{-}[Ru(L)X(H_2O)]^{2+} + X^- \quad (1)$$

$$trans\text{-}[Ru(L)X(H_2O)]^{2+} + Y^- \xrightarrow{\text{fast}} trans\text{-}[Ru(L)XY]^+ + H_2O \quad (2)$$

Reactions were carried out in *p*-toluenesulfonic acid (1–3 M) and NaX (1–3 M). The behavior of the bromide substitution of *trans*-$[Ru(teta)Cl_2]^+$ ($[H^+] = [Br^-] = 3.0$ M) at 80 °C can be taken as representative for this class of reactions. Initially, an isosbestic point was maintained at 405 nm for about 2 half-lives and a new set of isosbestic points gradually appeared at 416 and 360 nm, which were maintained until the end of the reaction. The initial and final spectra are identical with those of the authentic samples of *trans*-$[Ru(teta)Cl_2]^+$ and *trans*-$[Ru(teta)Br_2]^+$, respectively, in the same reaction medium of 3 M HBr. The behavior is fully consistent with the stoichiometric reactions (3) and (4). The kinetics for reaction

$$trans\text{-}[Ru(teta)Cl_2]^+ + Br^- \rightarrow trans\text{-}[Ru(teta)ClBr]^+ + Cl^- \quad (3)$$

$$trans\text{-}[Ru(teta)ClBr]^+ + Br^- \rightarrow trans\text{-}[Ru(teta)Br_2]^+ + Cl^- \quad (4)$$

3 was followed spectrophotometrically at the wavelength (360 nm) corresponding to an isosbestic point of the second step, and first-order rate constants were calculated from the standard semilogarithmic plots of the changing absorbance data, which were linear to 3 half-lives. The rate constants were found to be independent of acid (1.0–3.0 M), halide (1.0–3.0 M), and complex ($(1.0–4.0) \times 10^{-4}$ M) concentrations. These data are collected in Table I. Activation parameters were calculated from the Eyring plots of ln (k/T) vs. $1/T$ by the method of least squares.

The substitution reaction of *trans*-$[Ru(cyclam)Br_2]^+$ in 3 M HCl was complicated by dehydrogenation at a later part of the reaction. Hence only an approximate rate constant was estimated at 102.0 °C for comparison purposes.

(2) Kinetics of Base Hydrolysis of *trans*-$[Ru(L)ACl]^+$ (L = teta, tetb, or cyclam; A = OH or Cl). The base hydrolysis of *trans*-$[Ru(L)Cl_2]^+$ (L = teta and tetb) in NaOH was too fast to follow the repetitive spectral scans using a Unicam SP8000 recording spectrophotometer. Volhard's titration confirmed the release of both coordinated chlorides within 1 min on dissolving the complexes in 0.05 M NaOH at room temperature. With use of the stopped-flow spectrophotometer, two distinct steps could be clearly detected. These observations suggested that the base hydrolysis of *trans*-$[Ru(L)Cl_2]^+$ follows reactions 5 and 6. The stereoretentive nature of the reactions

$$trans\text{-}[Ru(L)Cl_2]^+ + OH^- \rightarrow trans\text{-}[Ru(L)OHCl]^+ + Cl^- \quad (5)$$

$$trans\text{-}[Ru(L)OHCl]^+ + OH^- \rightarrow trans\text{-}[Ru(L)(OH)_2]^+ + Cl^- \quad (6)$$

was confirmed by allowing a known solution of *trans*-[Ru-

Table I. First-Order Rate Constants, k_1, for the Reactions

$$trans\text{-}[Ru(L)X_2]^+ + Y \xrightarrow{k_1} trans\text{-}[Ru(L)XY]^+ + X$$

L	X	Y	θ/°C	$10^4 k_1$[a]/s^{-1}
teta	Cl	Br	70.8	$0.13_0 \pm 0.008$
			80.6	$0.53_3 \pm 0.02$
			86.5	$1.2_0 \pm 0.08$
			95.4	$3.7_0 \pm 0.20$
teta	Br	Cl	56.1	$0.23_0 \pm 0.01_5$
			61.4	$0.60_0 \pm 0.02$
			66.9	$1.3_0 \pm 0.08$
			71.8	$2.5_0 \pm 0.10$
			76.0	4.60 ± 0.20
tetb	Br	Cl	50.0	$1.8_5 \pm 0.10$
			59.1	$7.5_5 \pm 0.20$
			64.7	$18._5 \pm 1.0$
			70.0	$43._5 \pm 2.0$
cyclam	Br	Cl	102.0	~0.1

[a] Values of k_1 are independent of complex concentration ((1.0×10^{-4})–(4.0×10^{-4}) M), acid strength (1.0–3.0 M), halide concentration (1.0–3.0 M), and ionic strength (1.0–3.0 M). Each entry represents an average of two to four independent determinations.

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Table II. Second-Order Rate Constants, k_2, at 25.0 °C for the Base Hydrolysis of Some *trans*-$[Ru(L)Cl_2]^+$ and *trans*-$[Ru(L)(OH)Cl]^+$ Complexes at $I = 0.10$ M[a]

complex	$k_2/M^{-1}\ s^{-1}$
$[Ru(cyclam)Cl_2]^+$	1.1×10^2 [b]
$[Ru(teta)Cl_2]^+$	$(2.4 \pm 0.2) \times 10^3$
$[Ru(tetb)Cl_2]^+$	$(9.1 \pm 0.6) \times 10^3$
$[Ru(cyclam)(OH)Cl]^+$	$(2.2 \pm 0.4) \times 10^{-2}$
$[Ru(teta)(OH)Cl]^+$	7.6 ± 0.5
$[Ru(tetb)(OH)Cl]^+$	$(4.0 \pm 0.3) \times 10$

[a] Ionic strength was maintained with sodium *p*-toluenesulfonate. [b] Reference 10.

$(L)Cl_2]^+$ to proceed to completion and then acidifying it with concentrated HCl. The resulting solution was warmed and the final spectrum measured. It was found that the final spectrum was identical with that of the corresponding *trans*-$[Ru(L)Cl_2]^+$. Since reaction 6 is much slower than reaction 5, both steps could be conveniently followed without much interference. The teta complex was followed at 380 nm and tetb analogue at 385 nm. Since it was known[15] that *trans*-$[Ru(L)Cl_2]^+$ easily undergoes aerial dehydrogenation in neutral or basic media, the reactions were followed by first dissolving the complex in 0.001 M *p*-toluenesulfonic acid. This acidic solution was then mixed with excess NaOH in the stopped-flow apparatus. The final hydroxide concentration was calculated from the known concentrations of the acid and the alkali before mixing. Acid–base titration was also carried out on selected samples to check the hydroxide ion concentrations. For each complex, the reaction was followed over a range of hydroxide ion concentrations ((5.0×10^{-3})–(4.0×10^{-2}) M) and plots of pseudo-first-order rate constants, k_{obsd}, which were straight to 3 half-lives, against $[OH^-]$ were linear and passed through the origin. Second-order rate constants, k_2, were obtained from the slopes by the method of least squares.

The first step for the base hydrolysis of *trans*-$[Ru(cyclam)Cl_2]^+$ has been reported previously.[10] Preliminary study showed that the second step was also stereoretentive. The reaction was slow enough to be followed by the conventional spectrophotometric technique with a Unicam SP 8000 spectrophotometer. However, the reaction was slightly complicated toward its end by a dehydrogenation reaction and rate constants were obtained by the Guggenheim method. Hence, the rate data reported were only accurate to about 20%. All these second-order rate constants at 25.0 °C are collected in Table II.

Discussion

Halide substitution rate data extrapolated to 25.0 and 102.0 °C and activation parameters for some *trans*-$[Ru(L)X_2]^+$ complexes are collected in Table III. The observation that k_1(teta) > k_1(cyclam) for both the dichloro and dibromo series of complexes clearly demonstrates steric acceleration for dissociative reactions of these complexes. The steric effect, as measured by the kinetic ratio of k_1(teta)/k_1(cyclam) (2.9×10^3 for the dichloro system) is on the same order of magnitude of, though slightly greater than, that of the cobalt(III) system[20] with the corresponding kinetic ratio of 0.85×10^3 measured at 25.0 °C. The latter system is well-known to react by a dissociative mechanism. In the tetb complexes, the two coordinated halides are sterically nonequivalent with the up-plane halide embraced by both *gem*-dimethyl groups. This halide would be even more sterically congested than that in the corresponding teta analogue. The observation that k_1(tetb) > k_1(teta) for the dibromo complexes is again fully consistent with a dissociative mechanism in which the up-plane bromide in the tetb complex is preferentially activated. The highly

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Table III. First-Order Rate Constants at 25.0 °C, k_1(25), and 102.0 °C, k_1(102), and Activation Parameters for the Simple Ligand Substitution Reactions of Some *trans*-Tetraammineruthenium(III) Complexes[a]

complex	$k_1(25)/s^{-1}$	$k_1(102)/s^{-1}$	$\Delta H_1^{\ddagger}$/ kJ mol^{-1}	$\Delta S_1^{\ddagger}$/ J K^{-1} mol^{-1}
$[Ru(NH_3)_4Cl_2]^+$ [b]	1.7×10^{-6}		91.2	−50
$[Ru(en)_2Cl_2]^+$	4.2×10^{-6} [b]		97.5	−21
	4.5×10^{-6} [c]		89.0	−49
(*R,S*)-$[Ru(2,3,2\text{-tet})Cl_2]^+$ [b]	4.8×10^{-7}		103	−20
$[Ru(cyclam)Cl_2]^+$ [b]		3×10^{-7}		
$[Ru(teta)Cl_2]^+$	6.0×10^{-9}	8.6×10^{-4}	141	70
$[Ru(cyclam)Br_2]^+$		$\sim 1 \times 10^{-5}$		
$[Ru(teta)Br_2]^+$	1.1×10^{-7}	1.4×10^{-2}	139	88
$[Ru(tetb)Br_2]^+$	1.9×10^{-6}	3.3×10^{-1}	143	124

[a] This work except as indicated. Data for teta and tetb systems were extrapolated to 102.0 °C in order to compare directly with those of the cyclam systems. [b] Reference 9. [c] Extrapolated from data given in ref 8.

positive entropies of activation for the teta and tetb reactions could be taken to represent a relaxation of steric constraints in a dissociative activated complex.[19,20] That $\Delta S_1^{\ddagger}$(tetb) is even more positive than $\Delta S_1^{\ddagger}$(teta) for the dibromo complexes is fully consistent with this concept. In the ground state of the molecules, the methyl groups are frozen in particular positions to avoid the maximum crowding with the axial bromide ligand. The removal of the bromide ligand allows free rotation of the methyl groups and relaxes the associated solvent structures. This kind of steric constraint relaxation is greater for the tetb complex, hence a greater $\Delta S_1^{\ddagger}$, than for the corresponding teta complexes since more frozen methyl groups are involved in the former. Extrapolation of the rate data to 25.0 °C allows a comparison with other known rate data of *trans*-$[Ru(L)Cl_2]^+$ to be made. For the sake of comparison, a rate constant of $2 \times 10^{-12}\ s^{-1}$ was tentatively estimated for *trans*-$[Ru(cyclam)Cl_2]^+$ at 25.0 °C with use of the same k_1(teta)/k_1(cyclam) ratio determined at 102.0 °C. A comparison of the reactivities between *trans*-$[Ru(en)_2Cl_2]^+$ and *trans*-$[Ru(cyclam)Cl_2]^+$ shows that the reduction in rates, a measure of the increased chelation and macrocyclic effects, is as great as 2×10^6. This is much greater than the corresponding reduction ratio of 3×10 for the corresponding cobalt(III)[21] and of 1×10^3 for the corresponding chromium(III)[22] systems.

Apparently, our conclusion seems to be in total contradiction with that presented for an associative mechanism by Fairhurst and Swaddle.[11] However, it should be noted that the separation of substitution mechanisms into associative or dissociative might not be very distinct in certain cases. Reactions range continuously in the extent of bond making relative to bond breaking in the activated complexes, from one extreme to the other, depending on the choice of metal centers, ligands, solvents, and other reaction conditions. For substitution reactions of octahedral ruthenium(III) amine complexes, it is possible that both dissociative and associative pathways are not greatly different in their free energies of activation. A change in a certain reaction condition may tip the balance. Work is now in progress to look for a suitable system in which both the dissociative and associative pathways are approximately equally probable.[23]

In reference to Table II, the observed steric acceleration of k_2(tetb) > k_2(teta) > k_2(cyclam) in both *trans*-$[Ru(L)ACl]^+$ (A = OH or Cl) systems clearly supports the proposed S_N1cB mechanism for the base hydrolysis of octahedral ruthenium-

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(III) amine complexes. The much greater reactivity of *trans*-$[Ru(L)Cl_2]^+$ than the corresponding *trans*-$[Ru(L)(OH)Cl]^+$, as measured by the ratio of their corresponding rate constants at 25.0 °C (L = cyclam, 5.0×10^3; L = teta, 3.2×10^2; and L = tetb, 2.3×10^2), also follows the same pattern as that of the well-studied *trans*-$[CO(L)Cl_2]^+$ and *trans*-$[Co(L)(OH)Cl]^+$ systems with the corresponding kinetic ratios of 1.5×10^4 (L = cyclam)[21,24] and 5.5×10^3 (L = $(en)_2$).[25]

Acknowledgment. We thank the Committee on Research and Conference Grants of the University of Hong Kong for support.

Registry No. $[Ru(teta)Cl_2]^+ClO_4^-$, 76792-47-1; $[Ru(teta)Br_2]^+ClO_4^-$, 76792-49-9; $[Ru(tetb)Cl_2]^+ClO_4^-$, 76705-22-1; $[Ru(tetb)Br_2]^+ClO_4^-$, 76705-24-3; $[Ru(cyclam)Br_2]^+Br^-$, 74202-83-8; $[Ru(cyclam)(OH)Cl]^+$, 85282-36-6; $[Ru(teta)(OH)Cl]^+$, 85282-37-7; $[Ru(tetb)(OH)Cl]^+$, 85317-75-5; Cl^-, 16887-00-6; Br^-, 24959-67-9.

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Contribution from the Departments of Chemistry, Stanford University, Stanford, California 94305, and Wayne State University, Detroit, Michigan 48202

Synthesis, Structure, and Magnetism of a New Type of π-Molecular Complex Containing Binuclear Copper(II) Complexes and Benzene: Bis[2,2-dimethyl-7-(phenylimino)-3,5,7-octanetrionato]dicopper(II)–Benzene and Bis[2,2-dimethyl-7-((4-nitrophenyl)imino)-3,5,7-octanetrionato]dicopper(II)–Bis(benzene)

JAMES F. WISHART,† CHRISTOPHER CECCARELLI,‡ RICHARD L. LINTVEDT,*‡ JEREMY M. BERG,† DAVID P. FOLEY,† TOM FREY,† JAMES E. HAHN,† KEITH O. HODGSON,*† and ROBERT WEIS†

Received September 7, 1982

The title compounds have been crystallized and examined by X-ray diffraction techniques. The structure of $Cu_2(PAAan)_2 \cdot C_6H_6$ consists of stacks of alternating bis[2,2-dimethyl-7-(phenylimino)-3,5,7-octanetrionato]dicopper(II), $Cu_2(PAAan)_2$, and benzene molecules in an ADAD... pattern. Crystal data are as follows: $C2/m$, $a = 19.001$ (9) Å, $b = 6.516$ (3) Å, $c = 15.802$ (6) Å, $\beta = 113.36$ (3)°, $R_1 = 0.044$, $R_2 = 0.058$. The structure of $Cu_2(PAApnan)_2 \cdot 2C_6H_6$ consists of benzenes positioned directly above and below the center of the bis(2,2-dimethyl-7-((4-nitrophenyl)imino)-3,5,7-octanetrionato]dicopper(II) molecule. These units are stacked in a DADDAD... pattern. Crystal data are as follows: $C2/c$, $a = 15.312$ (3) Å, $b = 10.399$ (2) Å, $c = 23.743$ (4) Å, $\beta = 91.82$ (1)°, $R_1 = 0.039$, $R_2 = 0.048$. In $Cu_2(PAAan)_2 \cdot C_6H_6$ the planes of the alternating benzenes and metal complexes are parallel and separated by 3.258 (2) Å. In $Cu_2(PAApnan)_2 \cdot 2C_6H_6$, the two benzenes and each complex molecule are effectively parallel (dihedral angle 1.4°) and separated by 3.262 (8) Å. The interplanar spacing between benzene molecules associated with different binuclear chelates within the same stack is 3.860 (8) Å. These values are consistent with those found in a great many organic π-molecular complexes and are indicative of a weak donor–acceptor interaction between the benzene and binuclear Cu(II) complex. In both compounds the copper atoms and the donor atoms are coplanar, and both compounds are diamagnetic at room temperature. These results support the conclusion that coplanarity is a structural prerequisite for optimal antiferromagnetic exchange.

Introduction

Several authors[1] have demonstrated relationships between molecular structure and magnetic exchange in binuclear copper(II) complexes. One family of such complexes consists of the bis(1,3,5-triketonato)dicopper chelates and their Schiff base derivatives.[2] Previous X-ray crystal structure determinations[3] of bis(1,3,5-triketonato)dicopper(II) complexes showed that these molecules contain one axial ligand per copper, resulting in displacement of the copper from the plane of the equatorial ligands in typical 5-coordinate fashion. Thus, all magnetic-exchange–structural studies on these compounds to date have contained the complicating factor that the coppers are not in the simplest site symmetry. In order to present the simplest case for magnetic exchange between the copper ions, one would prefer that the coppers and donor atoms be coplanar. The binuclear Cu(II) complexes prepared from 1,3,5-triketones in which one terminal carbonyl oxygen has been replaced by an aniline (or substituted aniline) nitrogen were isolated as very small crystals without adducting ligands. Thus, these binuclear complexes seemed an excellent class of compounds for structural–magnetic studies since it appeared likely that the two copper atoms and the six donor atoms were coplanar.

In order to determine the structure of a binuclear triketonate without axial ligation, two complexes, bis[2,2-dimethyl-7-phenylimino-3,5,7-octanetrionato]dicopper, $Cu_2(PAAan)_2$, and bis[2,2-dimethyl-7-((4-nitrophenyl)imino)-3,5,7-octanetrionato]dicopper, $Cu_2(PAApnan)_2$, were recrystallized from dichloromethane, chloroform, and benzene. Crystals of $Cu_2(PAAan)_2$ isolated from CH_2Cl_2 and $CHCl_3$ solutions proved to be twinned. However, both compounds form excellent crystals from benzene and both contain benzenes of crystallization. Interestingly, the stoichiometries of the two are different. The first crystallizes with one benzene per molecule, $Cu_2(PAAan)_2 \cdot C_6H_6$, and the second with two per molecule, $Cu(PAApnan)_2 \cdot 2C_6H_6$. Both are unusually stable with respect to loss of benzene.

†Stanford University.
‡Wayne State University.

(1) See, for example: Sinn, E. *Coord. Chem. Rev.* **1970**, *5*, 313. Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173 and references therein.
(2) Lintvedt, R. L.; Tomlonovic, B. K.; Fenton, D. E.; Glick, M. D. *Adv. Chem. Ser.* **1976**, *No. 150*, 407.
(3) (a) Lintvedt, R. L.; Glick, M. D.; Tomlonovic, B. K.; Gavel, D. P.; Kuszaj, J. M. *Inorg. Chem.* **1976**, *15*, 1633. (b) Guthrie, J. W.; Lintvedt, R. L.; Glick, M. D. *Ibid.* **1980**, *19*, 2949. (c) Blake, A. B.; Fraser, L. R. *J. Chem. Soc., Dalton Trans.* **1974**, 2554. (d) Heeg, M. J.; Mack, J. L.; Glick, M. D.; Lintvedt, R. L. *Inorg. Chem.* **1981**, *20*, 833.

0020-1669/83/1322-1667$01.50/0