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Influence of π Back-Bonding on the Reactivity of the Nitrosyl Group. Nitrosation of Activated Methylene Compounds via Nitrosyl–Ruthenium Complexes

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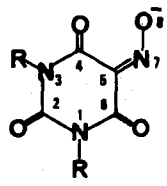
Received September 22, 1978

In an effort to probe the mechanism of nitrosation of activated methylene compounds through nitrosyl complexes, the reactions of a series of β-diketones with neutral nitrosyl–ruthenium complexes $Ru(AB)_2NOX$ have been investigated (AB is the monoanion of 2,4,6-trioxo-5-oximinopyrimidine or 1,3-dimethyl-2,4,6-trioxo-5-oximinopyrimidine; X = Cl, Br, OH, NO_2). The rate of the nitrosation reaction is strongly dependent on the acidity of the activated methylenes, the nature of the solvent, and the coordination environment of the nitrosyl group. The latter behavior is assessed in terms of the nitrosyl π^* acceptor orbital.

Nitrosyl ligand, as well as other ligands which contain metal–nitrogen multiple bonds, is of current interest. Structural[2-4] and synthetic[5] studies have shown the reactions of these ligands to be extremely varied. Whereas some nitrosyl complexes react as electrophiles,[6-10] others react as nucleophiles.[11-17] Because of the important role played by back-donation on the reactivity of coordinated nitrosyl, the development of a means to obtain quantitative information concerning the nature of metal-to-ligand π bonding has been of great interest in recent years.[13,14] N 1s bonding energy and NO stretching frequencies (or the derived force constant) of transition-metal nitrosyls have commonly been used to measure the degree of back-bonding.[4] There is a good correlation between ν(NO) frequencies and the electronic occupation of the π^* orbital of nitrosyl.[15] The nitrosyl complexes with high values of ν(NO) react with nucleophiles and the reactivity can be attributed to degree of NO^+ character.[8,10,16]

Earlier,[17,18] we reported the preparation and stereochemistry of new neutral ruthenium–mononitrosyl complexes *cis*-$Ru(AB)_2NOX$, where AB represents the unsymmetrical bidentate ligands 1,3-dihydrogenoviolurate, denoted H_2vi^-, or 1,3-dimethylviolurate, $dmvi^-$, and X represents Cl, Br, NO_2, OH, or monodentate AB.



R = R′ = H, 1,3-dihydrogenoviolurate, H_2vi
R = R′ = CH_3, 1,3-dimethylviolurate, dmvi

All these complexes possess nitrosyl groups with high ν(NO) stretching frequencies. The unusual reactivity of the nitrosyl complexes can be attributed to a considerable degree of NO^+ character in the formal (d^6) Ru(II)–NO^+ linkage caused by the relatively high formal oxidation state of the metal and the competitive back-bonding with the AB ligands. The effects of metal-to-ligand AB π back-bonding in $Ru(AB)_2NOX$ have been investigated by changes in ^1H NMR chemical shifts.[18] Moreover, in the case of $Ru(H_2vi)_2NOX$,[19] the capacity of the nitrosyl ligand to act as an electron pump[20,21] was demonstrated by a very important increasing of the acidity of the deprotonation sites in the coordinated heterocycle. The effects of H_2vi^-, Hvi^{2-}, and vi^{3-} as auxiliary ligands on the reactivity of the NO group of *cis*-$[Ru(H_pvi)_2NOCl]^{2p-4}$ ($2p$ = 0–4) with an activated methylene group to form N–C bonds attracted us to the present study. The formation of N–C bonds via intermediate ruthenium–nitrosyl complexes has been described in some instances,[9,22,23] and nitrosoarenes[24] and nitrosoalkanes[25] have proved to be interesting ligands of iron(II) porphyrins and hemoproteins. The present work is part of an effort meant to explore the mechanism of nitrosation of organic substrates via nitrosyl complexes.

Experimental Section

Materials. Barbituric acid (Merck), dimethylbarbituric acid (Fluka), dimedon, acetylacetone, ethyl acetoacetate, and diethyl malonate (Prolabo) were used without further purification.

Physical Measurements. UV–vis spectra were run on a Jobin and Yvon DUOSPAC 230 spectrophotometer using jacketed quartz cells. Infrared spectra were obtained on a Beckman IR20 AX with KBr plates and Nujol mulls. ^1H NMR spectra were taken on a Perkin-Elmer R 24 B. The potentiometric data were collected on a Radiometer PM 52 instrument employing a glass electrode (solution)|KCl (saturated solution) calomel electrode.

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Preparations of the Ruthenium–Nitrosyl Complexes. *cis*-Ru(dmvi)$_2$NOX and *cis*-Y$_{4-2p}$[Ru(H$_p$vi)$_2$NOCl] were prepared by following literature methods.[18,19]

Anal. Calcd for Ru(dmvi)$_2$NOCl, $RuC_{12}N_7O_9H_{12}Cl$: Ru, 18.90; C, 26.94; N, 18.33; H, 2.24; Cl, 6.64. Found: Ru, 18.75; C, 27.03; N, 18.43; H, 2.25; Cl, 6.84.

Anal. Calcd for Ru(H$_2$vi)$_2$NOCl, $RuC_8N_7O_9H_4Cl$: Ru, 21.10; C, 19.90; N, 20.50; H, 0.84; Cl, 7.42. Found: Ru, 20.85; C, 19.91; N, 20.5; H, 1.1; Cl, 7.42.

Anal. Calcd for Na$_2$[Ru(Hvi)$_2$NOCl], $RuC_8N_7O_9H_2ClNa_2$: Ru, 19.3; C, 18.4; N, 18.7; Cl, 6.8; Na, 8.8. Found: Ru, 19.1; C, 18.5; N, 19.1; Cl, 6.9; Na, 8.9.

Anal. Calcd for Ba$_2$[Ru(vi)$_2$NOCl], $RuC_8N_7O_9ClBa_2$: Ru, 13.5; C, 12.8; N, 13.1; Cl, 4.7; Ba, 36.6. Found: Ru, 13.3; C, 12.7; N, 13.2; Cl, 4.8; Ba, 37.0.

Ba$_{0.5}$[Ru(dmvi)$_2$(H$_2$vi)]. To a suspension of 0.1 g (0.187 mmol) of Ru(dmvi)$_2$NOCl in 20 mL of twice-distilled water was added 0.034 g of barbituric acid. The mixture was stirred for 24 h at 40 °C. A red compound was then precipitated from the deep red solution by slow addition of a saturated solution of $BaCl_2$. The resulting precipitate was collected and washed with C_2H_5OH and water. The compound was dried in vacuo over P_4O_{10} and then at 100 °C for 6 h under argon, yielding 0.11 g (85%). Anal. Calcd for $RuC_{16}N_9O_{12}H_{14}Ba_{0.5}$: Ru, 14.56; C, 27.68; N, 18.17; Ba, 9.91. Found: Ru, 14.3; C, 27.3; N, 17.8; Ba, 9.8.

The following products were prepared by using a similar procedure. However, for Ba$_{0.5}$[Ru(dmvi)$_2$N(O)acac] and Ba$_{0.5}$[Ru(H$_2$vi)$_2$N(O)acac] an excess of H$_2$acac (2 mmol) was necessary and a higher reaction temperature was used (60 °C).

Anal. Calcd for Ba$_{0.5}$[Ru(dmvi)$_2$N(O)dmo], $RuC_{20}N_7O_{11}H_{22}Ba_{0.5}$: Ru, 14.32; C, 34.02; N, 13.89; Ba, 9.71. Found: Ru, 14.1; C, 33.7; N, 13.9; Ba, 9.5.

Anal. Calcd for Ba$_{0.5}$[Ru(H$_2$vi)$_2$dmvi], $RuC_{14}N_9O_{12}H_{10}Ba_{0.5}$: Ru, 15.18; C, 25.23; N, 18.93; H, 1.50; Ba, 10.31. Found: Ru, 15.0; C, 25.1; N, 19.1; H, 1.7; Ba, 10.5.

Anal. Calcd for Ba$_{0.5}$[Ru(H$_2$vi)$_2$N(O)dmo], $RuC_{16}N_7O_{11}H_{14}Ba_{0.5}$: C, 29.25; N, 15.09; H, 2.15; Ba, 10.59. Found: C, 28.9; N, 15.4; H, 2.5; Ba, 10.7.

Anal. Calcd for Ba$_{0.5}$[Ru(dmvi)$_2$N(O)acac], $RuC_{17}N_7O_{11}H_{18}Ba_{0.5}$: C, 34.02; N, 13.89; Ba, 9.71. Found: C, 31.8; N, 14.5; Ba, 9.5.

Anal. Calcd for Ba$_{0.5}$[Ru(H$_2$vi)$_2$N(O)acac], $RuC_{13}N_7O_{11}H_{10}Ba_{0.5}$: C, 25.58; N, 16.07; H, 1.64; Ba, 11.26. Found: C, 25.1; N, 16.4; H, 1.8; Ba, 11.3.

Anal. Calcd for Ba$_{0.5}$[Ru(H$_2$vi)$_3$], $RuC_{12}N_9O_{12}H_6Ba_{0.5}$: Ru, 15.84; C, 22.58; N, 19.76; H, 0.94; Ba, 10.74. Found: Ru, 15.7; C, 22.1; N, 19.4; H, 1.5; Ba, 10.8.

Elemental analyses were undertaken by the microanalytical laboratory of C.N.R.S Thiais, France. Ruthenium analysis was performed by a method described in a previous work.[26,27]

Rate Measurements. The rate for the reaction of the coordinated nitrosyl group with barbituric acid, *cis*-[Ru(H$_p$vi)$_2$NOCl]$^{2p-4}$ + [H$_q$ba]$^{q-2}$ → --- ($2p$ = 0–4, q = 1, 2), was studied by spectrophotometry. Analytical concentrations in barbituric acid (B_T) and ruthenium (C_T) were fixed by measuring the requisite volumes of stock solutions:

$$C_T = \sum_{2p=0}^{4} [[Ru(H_pvi)_2NOCl]^{2p-4}] \text{ and } B_T = \sum_{q=1}^{2} [[H_qba]^{q-2}]$$

Ionic strength was fixed at 0.5 M with sodium chloride. Two hundred milliliters of an aqueous solution containing a buffer mixture of H$_2$ba and Hba$^-$ was degassed with argon and thermostated at 25 ± 0.1 °C. The stock solution of ruthenium nitrosyl was also degassed and equilibrated to 25.0 °C in the same water bath. For initiation of the reaction a known volume of ruthenium solution was syringed quickly into the flask. The circulation from the thermostated flask to the spectrophotometer cells was effected by a micropump. The reaction was followed at 495 nm to more than 95% completion in all cases. The pH was controlled during the reaction with variations of less than 0.01 for each run. For all of the runs, the barbituric acid concentration exceeded at least 40 times that of the Ru complex.

Calculations. If the reaction is a succession of steps of pseudo first order (reversible or nonreversible), the average molar absorptivity coefficient $\bar{\epsilon}(t)$ can always be represented by[28]

$$A(t)/C_T l = \bar{\epsilon}(t) = \epsilon_\infty + \sum_{i=1}^{n} [I_i \exp(-k_i^{obsd} t)]$$

Table I. Deprotonation Constants[a] of Compounds Containing an Acidic Methylene Group[29]

H$_2$am		deprotonation site	pK^H
	H$_2$ba	C$_5$	3.90
	H$_2$dmba	C$_5$	4.57
	H$_2$dmo	C$_2$	5.2
$CH_3COCH_2COCH_3$	H$_2$acac	C$_3$	8.8
$CH_3COCH_2COOC_2H_5$	H$_2$etaca	C$_3$	10.1
CH_3NO_2		C$_1$	10.2
$C_2H_5OCOCH_2COOC_2H_5$	H$_2$etm	C$_3$	~15

[a] At 25 °C and ionic strength μ = 0.5 M (NaCl).

where $A(t)$ is the absorbance at 495 nm at time t, l is the spectrophotometer cell length in centimeters, $\epsilon_\infty = A_\infty/C_T l$ (A_∞ is the final absorbance), ϵ_i is the molar extinction coefficient of species C$_i$, k_i^{obsd} is the pseudo-first-order rate constant of step i, and I_i is the constant function of ϵ_i and k_i^{obsd}.

First approximations of k_i^{obsd} and I_i values were obtained graphically. The best values of k_i^{obsd} and I_i were then obtained by using a least-squares refinement program that minimizes the $\sum_1^N(\bar{\epsilon}(obsd) - \bar{\epsilon}(calcd))^2$ function (N is the number of data points). The procedure computed simultaneously the best fit values of k_i^{obsd}, I_i, ϵ_∞, and also t_0, the correction on zero time, with their standard deviations. The final repartition of the residuals $|\bar{\epsilon}(obsd) - \bar{\epsilon}(calcd)|$ indicated the absence of systematic errors.

The reactions of the coordinated nitrosyl group in ruthenium complexes [Ru(H$_p$vi)$_2$NOCl]$^{2p-4}$ with barbituric species [H$_q$ba]$^{q-2}$ were studied over a wide range of pH. Using the known values of the equilibrium constants K_{2p} and K_q^H governing the deprotonations of the nitrosyl–ruthenium and barbituric species, respectively, we were able to evaluate the specific rate k_{2p} corresponding to the reaction of [Ru(H$_p$vi)$_2$NOCl]$^{2p-4}$ by using a least-squares calculation to fit the variation of k_1^{obsd} with pH (eq 3; vide infra).

Results

The Nitrosation Reactions. The reactions between the nitrosyl complexes and the organic compounds containing acidic methylene groups listed in Table I were tested.[29]

All of the neutral complexes *cis*-Ru(dmvi)$_2$NOX react fairly rapidly at room temperature with H$_2$ba, H$_2$dmba, H$_2$dmo, and H$_2$acac in acetonitrile, dimethylformamide, dimethyl sulfoxide, or water[30] to give the corresponding oxime complexes. The products Y[Ru(dmvi)$_2$N(O)am] were isolated by addition of the precipitating cation Y$^+$ = Ba$_{0.5}^+$, K$^+$, or P(Ph)$_4^+$ (depending on which gave the best yield) and were characterized by elemental analysis, infrared spectra, electronic spectra, and ^{1}H NMR spectra.

The easy nitrosation reaction is apparently limited to highly acidic methylene compounds, at least under mild conditions: no evidence for reaction of Ru(dmvi)$_2$NOCl on H$_2$etacac, CH_3NO_2, and H$_2$detm was observed after up to 2 h in aqueous or acetonitrile solution at room temperature. However, the addition of base caused the rapid formation of the oxime complexes: this reaction is not quantitative because hydroxide ion and organic compound are competing for Ru(dmvi)$_2$NOCl at a high pH value; the formation of the nitro complex [Ru(dmvi)$_2$(NO$_2$)Cl]$^{2-}$ was also detected.[31]

The rate of appearance of the deep red color after mixing Ru(dmvi)$_2$NOCl and H$_2$am increases with pH for all H$_2$am, and the relative order of the rates of nitrosation could be established by UV–visible observations using identical reaction

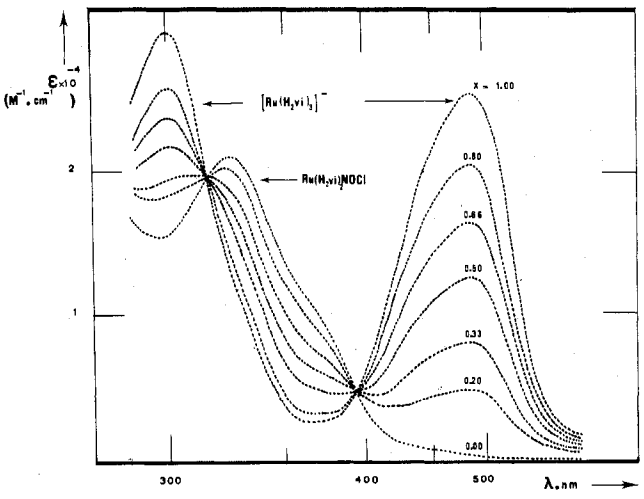


Figure 1. Electronic absorption spectral changes resulting from the addition of barbituric acid to a 3×10^{-4} M aqueous solution of $Ru(H_2vi)_2NOCl$, at pH 2.00, μ = 0.5 M (NaCl), and 25 °C. $x = B_T/C_T$.

conditions: $H_2ba \sim H_2dmba > H_2dmo \gg H_2acac > H_2etacac > CH_3NO_2 \sim H_2detm$. Since $Ru(dmvi)_2NOCl$ is not subject to acid–base reactions, the increase of reactivity with pH can only be caused by ionization of the acidic methylene group. Unfortunately, $Ru(dmvi)_2NOCl$ is quasi-insoluble in water, and quantitative measurement is very difficult. The reaction rate is strongly dependent on the rate of dissolution and depends on the dielectric constant and basicity of the solvent. $Ru(H_2vi)_2NOCl$ is highly soluble in water and so is better suited for quantitative study by spectrophotometry in aqueous solution. In an acidic pH range, the reactions of $Ru(H_2vi)_2NOCl$ are analogous with those of $Ru(dmvi)_2NOCl$: only the more acidic H_2ba, H_2dmba, H_2dmo, and H_2acac react and give $Y[Ru(H_2vi)_2N(O)am]$ products which we isolated in the same manner by introducing a precipitating cation $Y^+ = Ba_{0.5}^+$ or K^+ and characterized by elemental analysis, infrared spectra, electronic spectra, and ^1H NMR spectra. It is to be noted that $[Ru(H_2vi)_2N(O)ba]^-$ is in fact $[Ru(H_2vi)_3]^-$ and that this complex can be isolated by very slow crystallization of the reaction mixture in the form of $[H_3O^+][Ru(H_2vi)_3]\cdot 3H_2O$. A recent radiocrystallographic study[32] of this compound established the molecular structure and confirmed the tris-chelate molecular structure with three equivalent ligands in the *fac* configuration. Under identical conditions, the relative order of the rates of nitrosation was found to be $H_2ba \sim H_2dmba > H_2dmo \gg H_2acac$. However, unlike $Ru(dmvi)_2NOX$, no reaction between $Ru(H_2vi)_2NOCl$ and any compound of Table I can be detected in basic medium at room temperature: this fact clearly indicates that the deprotonation of coordinated violurate is unfavorable to the nitrosation reaction. Spectrophotometric titrations confirmed in the reaction of $Ru(H_2vi)_2NOCl$ with H_2ba a 1:1 stoichiometry (Figure 1). A pH decrease was noted during the nitrosation; an alkali titration proved the liberation of two protons for 1 mol of ruthenium complex. So the overall stoichiometry is

$$cis\text{-}Ru(AB)_2NOCl + H_2am \rightarrow [Ru(AB)_2N(O)am]^- + 2H^+ + Cl^-$$

In the particular case where AB = H_2vi and $H_2am = H_2ba$

$$cis\text{-}Ru(H_2vi)_2NOCl + H_2ba \rightarrow fac\text{-}[Ru(H_2vi)_3]^- + 2H^+ + Cl^-$$

It should be noted that $Ru(AB)_2N(O)am$ can also be prepared directly by the method described for 2,2′-bpy complexes of ruthenium.[9] The reaction then proceeds via a labile solvent-bound intermediate generated by the action of azide ion or hydroxylamine on the activated nitrosyl complex:

$$cis\text{-}Ru(AB)_2NOCl + N_3^- + solv \rightarrow [Ru(AB)_2(solv)Cl]^- + N_2 + N_2O$$

$$[Ru(AB)_2(solv)Cl]^- + [N(O)am]^- \rightarrow [Ru(AB)_2N(O)am]^- + Cl^- + solv$$

solv is acetonitrile or water

Table II. Observed Rate Constants[a] in the Nitrosation of Barbituric Acid by $[Ru(H_pvi)_2NOCl]^{2p-4}$

pH	10^5C_T, M	10^3B_T, M	k_1^{obsd}/B_T, $s^{-1}\ M^{-1}$	k_2^{obsd}, s^{-1}
2.07	3.33	1.5	0.70 (1)	1.5 (1)
2.31	3.27	1.5	0.99 (1)	1.6 (1)
2.45	3.33	1.5	1.14 (1)	1.3 (2)
2.84	3.30	1.0	1.47 (2)	1.1 (6)
2.83	3.47	1.5	1.45 (2)	1.2 (5)
2.85	3.35	2.0	1.43 (2)	1.4 (4)
2.84	3.41	2.5	1.46 (2)	1.3 (1)
2.82	3.32	5.0	1.42 (3)	1.2 (4)
2.86	3.44	15.0	1.44 (4)	1.3 (5)
3.09	3.33	1.5	1.56 (1)	1.4 (1)
3.40	3.11	1.5	1.38 (1)	1.3 (1)
3.65	3.32	1.5	1.24 (1)	1.25 (6)
3.89	3.33	1.5	0.882 (7)	1.1 (2)
4.00	3.30	1.5	0.684 (3)	1.61 (5)
4.14	3.34	1.5	0.547 (3)	1.18 (3)
4.18	3.20	1.5	0.587 (6)	1.13 (3)

[a] At 25 °C and ionic strength μ = 0.5 M (NaCl): the estimated standard deviations in the least significant figures are given in parentheses in this and all subsequent tables.

Kinetics. A quantitative kinetic study of the reaction between $Ru(H_2vi)_2NOCl$ and H_2ba was undertaken by spectrophotometric measurements at 495 nm. For all the experiments, the $\bar{\epsilon}(t)$ data are in good agreement with an equation of the form

$$\bar{\epsilon}(t) = \epsilon_\infty + I_1 \exp(-k_1^{obsd}t) + I_2 \exp(-k_2^{obsd}t) \quad (1)$$

The k_i^{obsd} values obtained by least-squares evaluation are listed in Table II with appropriate standard deviations. When the best values of I_1, I_2, k_1^{obsd}, k_2^{obsd}, and ϵ_∞ are used, $\sum_1^N[(\bar{\epsilon}(obsd) - \bar{\epsilon}(calcd))/\bar{\epsilon}(calcd)]$ is less than 0.5% for at least 90% of the reaction, the number of data points being greater than 60 for each determination. The two observed steps in the experimental nitrosation rate are consistent with the assumption of two consecutive processes, the second one being reversible or not:

$$\boxed{C_1} \xrightarrow{k_1^{obsd}} C_2 \underset{}{\overset{k_2^{obsd}}{\rightleftharpoons}} C_3$$

The starting material is framed, with $[C_1] = \sum_{2p=2}^{4}[Ru(H_pvi)_2NOCl]^{2p-4}$. At 495 nm those complexes all have negligible absorption. C_2 is one absorbing intermediate and C_3 is *fac*-$[Ru(H_2vi)_3]^-$. If the second step is reversible, $k_2^{obsd} = k_2 + k_{-2}$, where k_2 and k_{-2} correspond to the forward and reverse rate constants, respectively. The resolution of the differential equations leads to the concentration of the species $C_1(t)$, $C_2(t)$, and $C_3(t)$.[28] The initial conditions $C_1(0) = C_t$, $C_2(0) = 0$, and $C_3(0) = 0$ give for the average molar extinction coefficient an expression similar to (1) with

$$\epsilon_\infty = \frac{\epsilon_2 k_{-2} + \epsilon_3 k_2}{k_2 + k_{-2}} \quad (2)$$

$$I_1 = \frac{\epsilon_3 k_2 + \epsilon_2 k_{-2} - \epsilon_2 k_1^{obsd}}{k_1^{obsd} - k_2 - k_{-2}} \quad (3)$$

$$I_2 = \frac{(\epsilon_2 - \epsilon_3)k_1^{obsd} k_2}{(k_1^{obsd} - k_2 - k_{-2})(k_2 + k_{-2})} \quad (4)$$

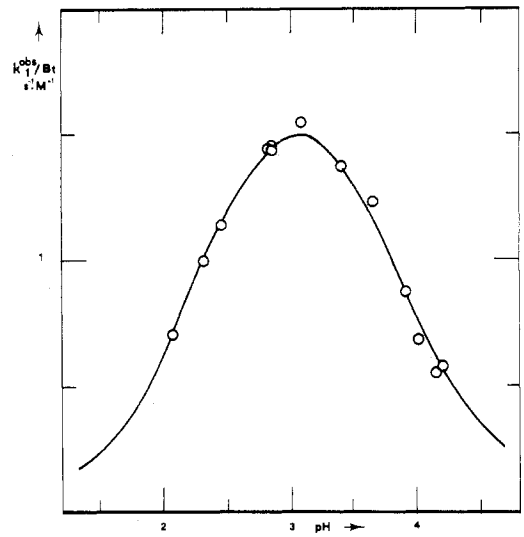


Figure 2. (○) Dependence of experimental first-order rate constants k_1^{obsd}/B_T on pH. (—) Curve calculated from eq 3 with the best values for $k_{1,2p}$.

Table III. Deprotonation Constants[a] of $Ru(H_2vi)_2NOCl$[19]

compd	2p	deprotonation site	pK_{2p}
$Ru(H_2vi)_2NOCl$	4	N_1	2.3 (1)
$[Ru(H_2vi)(Hvi)NOCl]^-$	3	N_1	3.5 (1)
$[Ru(Hvi)_2NOCl]^{2-}$	2	N_3	8.9 (1)
$[Ru(Hvi)(vi)NOCl]^{3-}$	1	N_3	10.2 (2)

[a] At 25 °C and μ = 0.5 M (NaCl).

Plots of k_1^{obsd} vs. B_T for a constant value of pH are linear at least over the experimental range studied ((1.0–15.0) × 10^{-3} M^{-1}), indicating for the first step a first order in barbituric acid. It should be noted that, in the conditions used, there can be no replacement of coordinated Cl^- by H_2O in $[Ru(H_pvi)_2NOCl]^{2p-4}$; the chloro complexes are indeed isolated in the same medium without detection of aquation reactions.

Nitrosyl Reactivity. As previously indicated in the qualitative study of nitrosation, reaction rates are strongly dependent on pH value: variation of k_1^{obsd}/B_T with pH (Figure 2) confirms that observation, and the interpretation of that plot can lead us to understanding the mechanism of the reaction. The form of the ruthenium–nitrosyl complex $Ru(H_2vi)_2NOCl$ changes with pH[19] by deprotonation of the coordinated heterocycles on the N_1 and N_3 sites to give anionic species $[Ru(H_pvi)_2NOCl]^{2p-4}$ with 2p = 0–4 (Table III).

In the pH range where the nitrosation reaction is measurable (pH 1.5–5.5), only three species are present in the solution with notable concentrations:

$$\underset{C_{14}}{[Ru(H_2vi)_2NOCl]^0} \overset{K_4}{\underset{H^+}{\rightleftharpoons}} \underset{C_{13}}{[Ru(H_2vi)(Hvi)NOCl]^-} \overset{K_3}{\underset{H^+}{\rightleftharpoons}} \underset{C_{12}}{[Ru(Hvi)_2NOCl]^{2-}}$$

Since the acidity constant of barbituric acid is in the same range (pH 3.9), the first step of the nitrosation reaction can be schematized as in Scheme I.

Two mechanisms can explain the form of the plot of Figure 2: mechanism A in which the deprotonated form of barbituric acid is the active one but the reactivities of nitrosyl complexes are in the $C_{14} > C_{13} > C_{12}$ order and mechanism B in which the H_2ba neutral form is active with reactivities in the reverse order. If the specific rate constants k_{12}, k_{13}, and k_{14} of the three nitrosyl complexes are assumed to be independent of pH,

Scheme I

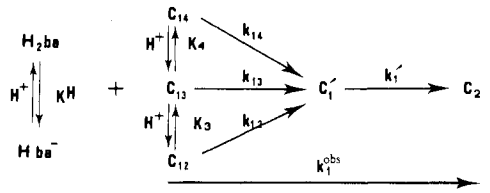


Table IV. Specific Rate Constants for the Nitrosation of Barbituric Acid by $[Ru(H_pvi)_2NOCl]^{2p-4}$

nitrosyl complexes $C_{1,2p}$	ν(NO), cm^{-1}	spec rate const[d] $k_{1,2p}$, s^{-1} M^{-1}
cis-$[Ru(H_2vi)_2NOCl]^0$	1950[a]	63.3 (1)
cis-$[Ru(H_2vi)(Hvi)NOCl]^-$		4.1 (1)
cis-$[Ru(Hvi)_2NOCl]^{2-}$	1910[b]	0.1 (1)
cis-$[Ru(Hvi)(vi)NOCl]^{3-}$		~0
cis-$[Ru(vi)_2NOCl]^{4-}$	1885[c]	~0
cis-$[Ru(dmvi)_2NOCl]^0$	1912[a]	

[a] ν(NO) measured in solid state. [b] ν(NO) measured as sodium salt. [c] ν(NO) measured as barium salt. [d] At 25 °C and μ = 0.5 M (NaCl).

a steady-state treatment on intermediate C_1' gives for mechanism A

$$k_1^{obsd}/B_T = \frac{K^H}{K^H + [H^+]} \frac{k_{14}[H^+]^2 + k_{13}K_4[H^+] + k_{12}K_3K_4}{[H^+]^2 + K_4[H^+] + K_3K_4} \quad (5)$$

where the limits for low and high values of pH are zero and k_{12}, respectively, and for mechanism B

$$k_1^{obsd}/B_T = \frac{[H^+]}{K^H + [H^+]} \frac{k_{14}[H^+]^2 + k_{13}K_4[H^+] + k_{12}K_3K_4}{[H^+]^2 + K_4[H^+] + K_3K_4} \quad (6)$$

where the limits for low and high values of pH are k_{14} and zero, respectively.

It should be noted that the existence of reverse reaction $C_1' \xrightarrow{k_{-1}} C_1$ introduces into the equation $k_1'/(k_1' + k_{-1})$ factors which are assumed to be independent of pH. Qualitative observations permit us to choose between the two mechanisms: at pH 0, no evidence of oxime formation can be detected even after a very long time but for a high pH value (pH >5.5) a slow reaction is indeed observable, that is consistent with the validity of the A mechanism. Furthermore, all the experiments with dimethylviolurato complexes point to the same conclusion. The data of Table II were treated by least-squares procedures and k_{14}, k_{13}, and k_{12} were computed by using eq 3.

For higher pHs, the reaction was too slow for good determination of $k_{1,2p}$ values; furthermore, variations of spectra due to deprotonation of $[Ru(H_2vi)_3]^-$[31] perturb the spectrophotometric measurements. Figure 2 shows the theoretical curve calculated by using these specific rate constants and the known values of K_3, K_4, and K^H (Tables I and III). It appears from the convergence of the experimental points with the calculated curve that the data are fully accounted for by the simple assumptions made.

Ring Closing. The effects on the variation of pH on the k_2^{obsd} values, listed in Table II, are too small to propose an extensive interpretation; the $[H^+]$ dependence can be assimilated to the standard deviation in the fitting procedure. Nevertheless k_2^{obsd} seems to decrease very slowly as the pH is raised, reaching rapidly a limiting value when pH > 2, and seems then independent of the two parameters $[H^+]$ and B_T; the effects of the variation of the chloride ion concentration were not studied. It is not possible, with these experimental data, to obtain the ring-closing mechanism: many of the

published works[33,35] describe a dissociative mechanism for octahedral complex substitution in ring closing and ring opening with a five-coordinate intermediate:

$$C_2 \underset{k_{-2}'}{\overset{k_2'}{\rightleftharpoons}} C_2' \xrightarrow{k_2''} C_3 \qquad k_2^{obsd} = \frac{k_2' k_2''}{k_{-2}'(Cl) + k_2''}$$

Unless the reaction is studied in the presence of high concentrations of acid and with strong ligand,[36] only the tris chelate can be detected when the reaction reaches equilibrium. Indeed, the back-reaction does not make any contribution to the approach to equilibrium. A steady-state treatment using that assumption leads to rate law 7. If $k_{-2}'(Cl)$ is much

$$k_2^{obsd} = k_2' k_2''(k_{-2}'(Cl) + k_2'')^{-1} \qquad (7)$$

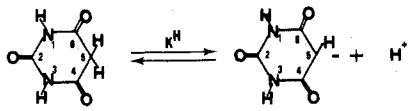
smaller than k_2'', (7) reduces to $k_2^{obsd} = k_2' = (1.3 \pm 0.2) \times 10^{-4}\ s^{-1}$.

The variation of I_1 and I_2 with k_1^{obsd} and k_2^{obsd} is in accordance with the theoretical expression and gives ϵ_2 22 400 $cm^{-1}\ M^{-1}$, the value of the extinction coefficient of the intermediate C_2.[37]

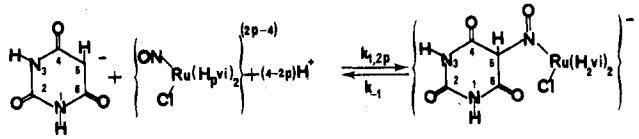
Discussion

The stoichiometric, X-ray,[32] and stereochemical experiments indicate the formation of N–C bonds between ruthenium–nitrosyl complexes and organic substrates containing the activated methylene group. The overall reaction involves several steps, and the mechanism suggested by the rate laws and stereochemical studies in the nitrosation reaction of barbituric acid H_2ba with *cis*-$Ru(H_2vi)_2NOCl$ can be diagrammed as follows.

The fast equilibrium

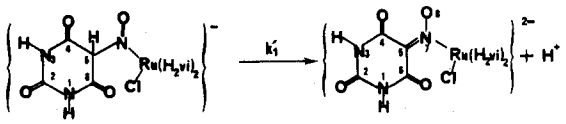


gives barbiturate anion Hba^-, whose nucleophilic carbon C_5 attacks the nitrosyl ligand at its electron-deficient nitrogen:



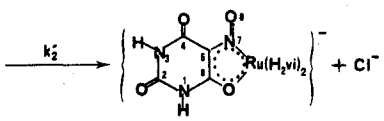
C-nitrosation

The nitroso complex can easily lose a proton to give an oximato complex:



C-oximation

Finally, the chelate ring-closing reaction occurs with loss of chloride anion:



We were unable to obtain direct evidence for a Lewis acid–base adduct where the base Hba^- is bound to the nitrogen of the nitrosyl group, but this reaction seems formally similar to the reactions of activated nitrosyl complexes on bases such as OH^-,[38] N_3^-, NH_2OH, ...,[39,40] and aromatic amines.[10]

Although linkage in barbiturate complexes of ruthenium occurs thanks to oxygen[41] and the formal charges of O_2, O_4, and O_6 atoms are greater than that of the C_5 atom,[42] it is logical to assume that the nitrogen atom links with the C_5 carbon of Hba^- rather than the oxygen site on the enolate ion.[43] Moreover, it is also logical to assume, in the first step, a fast proton transfer to the N_1 and N_3 sites of the heterocycles in the pH range studied (pH 1.5–5.5): the formation of adduct decreasing the back-donation $d\pi \rightarrow \pi^*$ NO must increase electron density at remote ligand sites; indeed in the tris chelates, the deprotonations occur at far higher pH values.[31]

The second step in the nitrosation reaction involves deprotonation at the C_5 site of the adduct to give an oximato complex.[44,45] It was not possible in the kinetic calculations to separate the specific rate constant from this step which appears in the form $k_1'k_{1,2p}/(k_1' + k_{-1})$. If the proton transfer is fast or if the reverse reaction is very slow or absent, this reduces to $k_{1,2p}$. The low value of the rate constant of k_2' ring closing can be explained either by the inertness to substitution reactions of Ru(II) complexes[46] or by the great concentration of chloride anion.[34] Because of the great stability of the tris-chelated complex *fac*-$[Ru(H_2vi)_3]^-$, the ring-opening reaction can never be observed under such experimental conditions. Ring opening can only occur with a very strong reactant such as nitrosonium ion[36] to regenerate the $Ru(AB)_2NOX$ complexes. A totally different mechanism was recently proposed[23] for the formation of organo nitrogen compounds between $PhCH_2Br$ and $Ru(NO)_2(PPh_3)_2$ under very hard conditions, but in this dinitrosyl complex, the value of ν(NO) suggests the presence of one bent

$$Ru{-}N\overset{O}{\diagdown}$$

The quantitative and qualitative kinetic results of the nitrosation reaction via the intermediacy of ruthenium–nitrosyl complexes $Ru(AB)_2NOX$ indicate that the rate of reaction is strongly dependent on the nature of the solvent, the acidity of activated methylene, and the coordination environment of the nitrosyl group.

Although the nature of the solvent is certainly an important parameter of the reaction rate, we have not investigated its influence quantitatively. The reactions can be performed in water, MeCN, Me_2SO, or DMF, which are all solvents with high dielectric constants: it is highly probable that the mechanism of the nitrosation is similar in these media.

The nitrosation reaction for barbituric acid occurs after loss of a proton and enolate formation: the rate is proportional to the enolate concentration, and high values of K^H and pH—which increase enolate concentration—also increase the rate of the nitrosation reaction. The preliminary enolate formation was demonstrated for cyclic β-diketones with strongly acidic methylene: H_2ba, H_2dmba, and H_2dmo in water.

A problem arises with the linear β-diketones, namely, acetylacetone chiefly in organic solvents.[47]

Reactivity of the Nitrosyl Group. In an appropriate coordination environment the nitrosyl group has been shown to react chemically like the nitrosonium ion.[9,10,16] In ruthenium–nitrosyl complexes *cis*-$Ru(AB)_2NOX$ the reactivity of the nitrosyl group depends on two factors: the nature of the cis-activating ligand X and the competition of $d\pi \rightarrow \pi^*$(NO) with $d\pi \rightarrow \pi^*$(AB) back-donation.

The effect of cis X on the reactivity of the nitrosyl group in $Ru(AB)_2NOX$ is comparable to that of $[Ru(bpy)_2NOX]^{2+}$ [16] and increases as the back-bonding ability of the cis ligands increases $NO_2 > Cl \sim Br > OH$.

The competitive $d\pi \rightarrow \pi^*$(NO) and $d\pi \rightarrow \pi^*$(AB) back-bonding was characterized in $Ru(AB)_2NOCl$ (AB = dmvi, H_2vi) by changes in ^1H NMR chemical shifts,[18] in ν(CO) frequencies of the coordinated heterocycles, and in the ν(NO) frequency of the nitrosyl group. The H–N_1 and H–N_3

sites of $Ru(H_2vi)_2NOCl$ are the best indicators of charge-density changes. The $H-N_1$ and $H-N_3$ ^1H chemical shifts indicate that electron-density depletion in the coordinated pyrimidine of *cis*-$Ru(H_2vi)_2NOCl$ is greater than in *fac*-$[Ru(H_2vi)_3]^-$.[18]

The charge withdrawal of Ru(II) and $d\pi \rightarrow \pi^*(NO)$ back-bonding enhances the acidity of the deprotonation sites N_1 and N_3 without compensation from $d\pi \rightarrow \pi^*(H_2vi)$ back-bonding.

The nitrosyl ligand absorbs electron density from a πd orbital, and back-bonding to another ligand using the same orbital will be weakened.

The deprotonation of coordinated heterocycles on N_1 and N_3 sites gives anionic isostructural nitrosyl species *cis*-$[Ru(H_pvi)_2NOCl]^{2p-4}$. The increasing negative charge enhances the σ donation to the metal from the heterocycles and therefore enhances the concomitant $d\pi \rightarrow \pi^*(NO)$ back-donation. For these compounds, with "linear" nitrosyl groups (an assumption using Haymore and Ibers' suggestions[48]), the electronic occupancy of the π^* orbital of nitrosyl can be assessed by the values of the $\nu(NO)$ frequency.[15] As expected, the $\nu(NO)$ frequency and the electron deficiency of the nitrogen atom decrease from $Ru(H_2vi)_2NOCl$ to $[Ru(vi)_2NOCl]^{4-}$ (Table IV).

This progressive deactivation of nitrosyl is well evidenced by kinetic study: only $Ru(H_2vi)_2NOCl$ and $[Ru(H_2vi)(vi)NOCl]^-$ react perceptibly with strongly acidic methylene groups at room temperature. At higher pH values, although the enolate formation is favored, the nitrosylation reaction rate decreases by formation of the less active anions $[Ru(Hvi)_2NOCl]^{2-}$, $[Ru(Hvi)(vi)NOCl]^{3-}$, and $[Ru(vi)_2NOCl]^{4-}$. Evidently $Ru(dmvi)_2NOCl$ does not undergo this deactivation with increasing pH and can react with all acidic methylene groups even in a basic medium. The electrophilic behavior of nitrosyl groups in the reaction with activated methylene compounds is fairly consistent with the $\nu(NO)$ predictions.[8] An electrophilic character remains nevertheless on the "deactivated" nitrosyl group, and $[Ru(vi)_2NOCl]^{4-}$ can be converted to the nitro complex by the action of an OH^- excess. As nitrosating agents for activated methylene systems, the nitrosyl complexes appear to be competitive with the nitrosonium ion if the nitrosyl group is sufficiently activated by the coordination sphere. It is also conceivable that reaction with less strongly acidic methylene compounds may occur by using a more highly activated nitrosyl or more drastic conditions.

Registry No. $Ru(dmvi)_2NOCl$, 69744-60-1; $Ru(H_2vi)_2NOCl$, 69744-61-2; $Na_2[Ru(Hvi)_2NOCl]$, 69779-04-0; $Ba_2[Ru(vi)_2NOCl]$, 69744-62-3; $Ba_{0.5}[Ru(dmvi)_2(H_2vi)]$, 69687-60-1; $Ba_{0.5}[Ru(dmvi)_2N(O)dmo]$, 69687-61-2; $Ba_{0.5}[Ru(H_2vi)_2dmvi]$, 69687-62-3; $Ba_{0.5}[Ru(H_2vi)_2N(O)dmo]$, 69687-63-4; $Ba_{0.5}[Ru(dmvi)_2N(O)acac]$, 69687-64-5; $Ba_{0.5}[Ru(H_2vi)_2N(O)acac]$, 69687-65-6; $Ba_{0.5}[Ru(H_2vi)_3]$, 69706-76-9; *cis*-$[Ru(H_2vi)(Hvi)NOCl]^-$, 69706-75-8; *cis*-$[Ru(Hvi)(vi)NOCl]^{3-}$, 69687-66-7; H_2ba, 67-52-7; H_2dmba, 769-42-6; H_2dmo, 126-81-8; H_2acac, 123-54-6; H_2etaca, 141-97-9; H_2etm, 105-53-3; CH_3NO_2, 75-52-5.

Supplementary Material Available: A listing of observed and calculated average molar absorption coefficients $\epsilon(t)$ from eq 1 (10 pages). Ordering information is given on any current masthead page.

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(29) The following abbreviations will be used throughout this paper: H_2am, compounds with an acidic methylene group; H_2ba, 1*H*,3*H*,5*H*-pyrimidine-2,4,6-trione or barbituric acid; H_2dmba, 1,3-dimethyl-5*H*-pyrimidine-2,4,6-trione or 1,3-dimethylbarbituric acid; H_2dmo, 5,5-dimethylcyclohexane-1,3-dione or dimedon; H_2acac, pentane-2,4-dione or acetylacetone; $H_2etacac$, ethyl acetoacetate; H_2etm, diethyl malonate; $[N(O)am]^-$, monoanion of oximes N(OH)am of the former, e.g., $[N(O)ba]^- \equiv H_2vi^-$, $[N(O)dmba]^- \equiv dmvi^-$, $[N(O)dmo]^-$, and so on.
(30) These ruthenium–nitrosyl complexes $Ru(dmvi)_2NOX$ are not significantly soluble in any of those solvents whereas the analogous complexes $Ru(H_2vi)_2NOX$ are. They are insoluble in water and the best solvent is generally Me_2SO.
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Strong π-Antibonding Effects on the Electronic Structures of Complexes with Charge-Delocalized Macrocyclic Ligands

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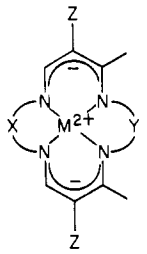
Received September 7, 1978

The complexes of copper(II) with the 14-, 15-, and 16-membered, charge-delocalized, dianionic macrocycles Me_2[14–16]tetraenatoN_4^{2-} exhibit a number of properties that are attributable to the presence of strong ligand–metal π interactions of an antibonding nature. These include d–d transitions in their electronic spectra, which occur at remarkably low energies, and the ESR spectral parameters for these compounds. The square-planar complexes show no tendency to add axial ligands in strongly coordinating solvents. The strong π-antibonding, as differentiated from π-bonding, interactions generate the distinctive qualities of these complexes. For example, the presence of low-energy vacant π orbitals in metal porphyrins contributes to their rich patterns of reduction. In contrast, the complexes of the class discussed here are difficult to reduce.

Introduction

The investigation of the effect of substituents on the electronic spectral and electrochemical properties of complexes having structure I has shown that the changes in electron



I

density that occur on the ligand are transmitted directly to the metal ion.[2] Thus the use of substituents affords a powerful technique for controlling the electronic character of the donor atoms without altering the stereochemistry of the coordination sphere. The possibilities opened by such control are well illustrated by the recent report that the presence of acetyl substituents on the γ-carbon atoms of bis(acetylacetone) ethylenediimine produces a cobalt(II) complex whose O_2 adduct is stable at room temperature.[3] This contrasts with the usual behavior of such Schiff base complexes since their O_2 adducts are generally formed only at low temperatures.[4] The unsubstituted macrocycles of structure I with Z = H may be viewed as the parents of all compounds having structure I.

This key role of these unsubstituted species causes us to be especially interested in their electronic structures. We report here the syntheses of the copper(II) complexes, $Cu^{II}(Me_2$[14–16]tetraenato$N_4)$, and the results of physical studies with emphasis on their electronic and ESR spectra. The complexes are unusual in that their electronic spectra exhibit d–d transitions at unusually low energies. The assignment of these bands leads to the conclusion that a very strong π interaction exists between the e_g orbitals of the metal ion and the filled ligand π orbitals. The assignments are entirely consistent with the results of ESR studies. Thus, the unsubstituted ligands of this class (structure I) are very strong π donors, as well as strong σ donors. This description of electronic structure also accounts for the relatively slight tendency of the four-coordinate planar complexes of these ligands to expand their coordination numbers. Previous studies have remarked on the difficulty of producing five- and six-coordinate structures by the addition of axial ligands.[5,6]

Table I. Visible Spectral Data (cm^{-1} (ε)) for $H_2(Me_2$[n]tetraenato$N_4)$ and $Cu(Me_2$[n]tetraenato$N_4)$[a]

$H_2(Me_2$[14]tetraenato$N_4)$	29 500 (sh, ~4000), 32 300 (30 100), 33 670 (27 200)
$H_2(Me_2$[15]tetraenato$N_4)$	30 300 (sh, ~6400), 33 560 (26 600)
$Cu(Me_2$[14]tetraenato$N_4)$	16 100 (165), 20 000 (sh, 200), 29 400 (32 200), 32 600 (26 900)
$Cu(Me_2$[15]tetraenato$N_4)$	13 300 (136), 18 100 (155), 27 000 (sh, 7100), 29 600 (26 900), 31 000 (9900)
$Cu(Me_2$[16]tetraenato$N_4)$	11 800 (215), 18 000 (200), 24 000 (2300), 28 800 (23 700), 31 000 (sh, 8400)

[a] n = 14, 15, and 16.

Results and Discussion

The procedures used in the synthesis of $Cu(Me_2$[14–16]-tetraenato$N_4)$ are unremarkable; however, the products require protection from the air. Elemental analyses, parent ion peaks in the mass spectra, and infrared spectra confirm the assigned structures.

The electronic spectra (chloroform solution) of the complexes show three features assignable as arising from d–d transitions (Table I). This includes two absorption bands in the region 10–20 $cm^{-1} \times 10^3$ and a third band that is partially obscured by strong intraligand and/or charge-transfer bands. By comparison of the spectra of the complexes with those of the neutral free ligands, $H_2(Me_2$[14,15]tetraenato$N_4)$, a band at about 24 $cm^{-1} \times 10^3$ is assigned as a d–d transition for $Cu(Me_2$[16]tetraenato$N_4)$ and one at about 27 $cm^{-1} \times 10^3$ for $Cu(Me_2$[15]tetraenato$N_4)$. The corresponding absorption is not resolved in the case of the 14-membered ring derivative. The spectra of $H_2(Me_2$[15]tetraenato$N_4)$ and $Cu(Me_2$[15]-tetraenato$N_4)$ are shown in Figure 1. Most notably, the d–d bands shift toward higher energy as the size of the macrocyclic ring decreases. On the basis of the shifts observed, the third band for $Cu(Me_2$[14]tetraenato$N_4)$ would be expected to occur at 29–33 $cm^{-1} \times 10^3$. This would place it in the same region

0020-1669/79/1318-1555$01.00/0