Activation Volumes for the Quintet/Singlet Relaxation Kinetics of Iron(II) Complexes

Sir:

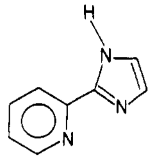
There has long been interest in the parameters that determine the equilibria and dynamics of "spin-crossover" complexes, a class of transition-metal compounds for which both high-spin and low-spin electronic states are accessible thermally. Examples include compounds of Fe(II), Fe(III), Co(II), and Co(III).[1,2] Among these are certain d^6 iron(II) species that exist at ambient conditions in solution as equilibrium mixtures of the quintet high-spin (HS) and singlet low-spin (LS) electronic isomers (eq 1; L is generally a polydentate nitrogen heterocycle ligand).[1]

$$\underset{\text{LS}}{{}^1[\text{FeL}_n{}^{2+}]} \underset{k_{\text{hs}}}{\overset{k_{\text{ls}}}{\rightleftharpoons}} \underset{\text{HS}}{{}^5[\text{FeL}_n{}^{2+}]} \tag{1}$$

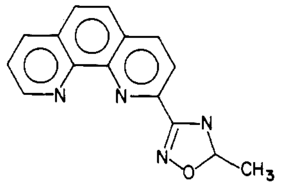
$$K = \frac{[\text{HS}]}{[\text{LS}]} = \frac{k_{\text{ls}}}{k_{\text{hs}}} \tag{2}$$

Additional interest in the intersystem crossing dynamics between the two states (eq 1) of such complexes derives in part from the question of how spin-relaxation processes and the related ligand-reorganization barriers may influence the kinetics of bimolecular electron-transfer reactions.[3] This process represents an ideal case for examination of the thermodynamic and activation parameters of the associated ligand rearrangement, given that the metal–ligand bonds in the HS isomer are about 0.1 Å longer than in the LS isomer.[4] Thus, partial molar volumes ($\Delta\bar{V}$) of the two spin states may differ by more than 10 cm³/mol for a particular complex.[5] While enthalpic and entropic barriers for the intersystem crossing have been elucidated from temperature dependencies of spin-relaxation lifetimes,[5–7] the corresponding activation volumes $\Delta V^{\ddagger}$ have not been previously described in print.[8] Here we report $\Delta V^{\ddagger}$ values obtained from the pressure dependencies of the spin-relaxation rates determined by pulse laser experiments.[9]

The two complexes $\text{Fe(pyim)}_3{}^{2+}$ (I) and $\text{Fe(phenmethoxa)}_2{}^{2+}$ (II) (pyim = 2-(2-pyridyl)imidazole, phenmethoxa = 3-(1,10-phenanthrol-2-yl)-5-methyl-1,2,4-oxadiazole) each exist in equilibrium between the two spin states (eq 1) with the equilibrium constants $K = 0.56$[10] and 5.38,[11] respectively, in acetone at 298 K (defined as in eq 2) and with differences in the partial molar volumes $\Delta\bar{V}$ of 8.1 and 12.3 cm³/mol,[12] respectively. Pulse laser excitation (532 nm) of each complex leads to transient bleaching of the strong charge-transfer bands of the LS isomer followed by first-order relaxation to the original spectrum with lifetimes (τ) of 45 ns for I and 110 ns for II in 298 K acetone. Given that the electronic excited states of polypyridyl complexes of Fe(II) have been shown to have very short lifetimes (<1 ns)[13] in fluid solution, the transient bleaching can be attributed to the formation of larger than equilibrium concentrations of the HS isomer as one deactivation pathway of the excited states. The processes seen here thus represent the spin equilibria relaxation dynamics. The lifetime measured for I is in agreement with that measured previously in acetonitrile/methanol by a temperature-jump experiment[6] as well as with another laser flash photolysis experiment in the same solvent.[7]



pyim



phenmethoxa

The data from pulse laser lifetime measurements over the pressure range 0.1–300 MPa, when plotted according to eq 3,[13]

$$\left(\frac{\delta \ln \tau^{-1}}{\delta P}\right)_T = -\frac{\Delta V_{\tau^{-1}}{}^{\ddagger}}{RT} \tag{3}$$

gave the $\Delta V_{\tau^{-1}}{}^{\ddagger}$ values of 0.0 ± 0.5 and 2.0 ± 0.5 cm³/mol for I and II, respectively. From these and the values of $\Delta\bar{V}$ and K, the activation volumes for the forward and reverse rates, $\Delta V_{\text{ls}}{}^{\ddagger}$ and $\Delta V_{\text{hs}}{}^{\ddagger}$, can be calculated from[14]

$$\Delta V_{\text{hs}}{}^{\ddagger} = \Delta V_{\tau^{-1}}{}^{\ddagger} - \frac{K}{1+K}\Delta\bar{V} \tag{4}$$

$$\Delta V_{\text{ls}}{}^{\ddagger} = \Delta V_{\tau^{-1}}{}^{\ddagger} + \frac{1}{1+K}\Delta\bar{V} \tag{5}$$

where $\tau^{-1} = k_{\text{hs}} + k_{\text{ls}}$ and $\Delta V_{\text{i}}{}^{\ddagger} = -RT(\delta \ln k_{\text{i}}/\delta P)_T$. The calculated values for $\Delta V_{\text{ls}}{}^{\ddagger}$ and $\Delta V_{\text{hs}}{}^{\ddagger}$ are 5.2 ± 2.0 and −2.9 ± 1.5 cm³/mol for $\text{Fe(pyim)}_3{}^{2+}$ and 3.9 ± 1.0 and −8.4 ± 2.0 cm³/mol for $\text{Fe(phenmethoxa)}_2{}^{2+}$. These and other parameters are summarized in Table I.

Although coordinates for the transition state can only be estimated from the activation energy and volume terms, it is clear that there are significant pressure effects on the HS → LS relaxation rates. The negative $\Delta V_{\text{hs}}{}^{\ddagger}$ values indicate that the volume of each activated complex is indeed substantially smaller than that of the respective high-spin isomer. Preliminary studies of other complexes related to II show similar effects. The results suggest that the geometric changes associated with the intersystem crossing under these conditions involve a radial compression of the metal–ligand bonds consistent with the theoretical treatments of Buhks et al.[15] and of Dose et al.[6] An alternative mechanism involving twisting of the ligand field[16] would be expected to show positive activation volumes for both k_{ls} and k_{hs} owing to the displacement of solvent molecules from the cavities between the chelate rings.[17]

---

(1) (a) Gutlich, P. *Struct. Bonding (Berlin)* **1981**, *44*, 83–202. (b) Goodwin, H. A. *Coord. Chem. Rev.* **1975**, *18*, 293–352.

(2) (a) Navon, G.; Klaui, W. *Inorg. Chem.* **1984**, *23*, 2722–2725. (b) Maeda, Y.; Tsutsumi, N.; Takashima, Y. *Inorg. Chem.* **1984**, *23*, 2440–2447. (c) Simmons, M. C.; Wilson, L. J. *Inorg. Chem.* **1977**, *16*, 126.

(3) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441–498 and references therein.

(4) (a) Katz, B. A.; Strouse, C. E. *J. Am. Chem. Soc.* **1979**, *101*, 6214; *Inorg. Chem.* **1980**, *19*, 658. (b) Sinn, E.; Sim, G.; Dose, E. V.; Tweedle, M. F.; Wilson, L. *J. Am. Chem. Soc.* **1978**, *100*, 3375.

(5) (a) Binstead, R. A.; Beattie, J. K.; Dewey, T. G.; Turner, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 6442. (b) Beattie, J. K.; Binsted, R. A.; West, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 3044.

(6) Dose, J. K.; Hoselton, M. A.; Sutin, N.; Tweedle, M. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 1141.

(7) McGarvey, J.; Lawthers, I. *J. Chem. Soc., Chem. Commun.* **1982**, 906.

(8) (a) This work was presented at the XXIIIrd International Conference on Coordination Chemistry, Boulder, CO, July 1984. (b) At the same conference, I. Lawthers, J. J. McGarvey, K. Heremans, and H. Toftlund also described similar experiments on related iron(II) compounds. Pressure effects on the relaxation rates of I in acetone were investigated by both groups, and the results agreed within experimental uncertainty.

(9) (a) The relaxation lifetime measurements were made with the use of a Nova Swiss high-pressure solution cell modified for excited-state-absorption ESA) measurements.[9b] The cell was fitted internally with Suprasil quartz light guides, which give an excellent cross section for ESA. The complex was excited with a 532-nm pulse (about 10 ns) from a doubled Nd/YAG laser, and optical density changes in the sample were monitored at right angles by using a 300 Xe lamp as a light source coupled through a set of Spex monochromators (before and after the cell) to a fast-response PMT (RCA 8852) and a Tektronix Model WP 2110 transient digitizer system. (b) Weber, W.; DiBenedetto, J.; Offen, H.; van Eldik, R.; Ford, P. C. *Inorg. Chem.* **1984**, *23*, 2033–2038.

(10) Reeder, K. A.; Dose, E. V.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 1071.

(11) Determined by the Evans NMR method (Evans, D. F. *J. Chem. Soc.* **1959**, 2003).

(12) The $\Delta\bar{V}$ values for I and II were determined from the pressure effects on the absorption spectra over the range 0.1–300 MPa.[5a]

(13) Creutz, C.; Chau, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309.

(14) Weber, W.; van Eldik, R.; Kelm, H.; DiBenedetto, J.; Ducommun, Y.; Offen, H.; Ford, P. C. *Inorg. Chem.* **1983**, *22*, 623.

(15) Buhks, E.; Navon, G.; Bixon, M.; Jortner, J. *J. Am. Chem. Soc.* **1980**, *102*, 2918.

(16) (a) Purcell, K. F. *J. Am. Chem. Soc.* **1979**, *101*, 5147. (b) Vanquickenborne, L. G.; Pierloot, K. *Inorg. Chem.* **1981**, *20*, 3673 and references therein.

(17) Lawrance, G. A.; Stranks, D. R. *Inorg. Chem.* **1977**, *16*, 929; **1978**, *17*, 1804.

0020-1669/85/1324-0455$01.50/0

Table I. Activation and Thermodynamic Parameters for the Spin Relaxation of the Quintet/Singlet Equilibria of $Fe(pyim)_3^{2+}$ and $Fe(phenmethoxa)_2^{2+}$ in Acetone

param	units	$Fe(pyim)_3^{2+}$	$Fe(phenmethoxa)_2^{2+}$
K (25 °C)		0.56 ± 0.18	5.4 ± 2.0
τ	ns	45 ± 5	110 ± 10
ΔH°	kcal/mol	3.8 ± 0.1[a]	5.7 ± 0.1
ΔS°	cal/K·mol	11.6 ± 0.3[a]	22.5 ± 0.5
$\Delta \overline{V}$	cm^3/mol	8.1 ± 1.3	12.3 ± 1.0
$\Delta V_{\tau^{-1}}^{\ddagger}$	cm^3/mol	0.0 ± 0.5	2.0 ± 0.3
$\Delta H_{ls}^{\ddagger}$	kcal/mol	6.7 ± 0.3	7.8 ± 0.4
$\Delta H_{hs}^{\ddagger}$	kcal/mol	2.9 ± 0.3	2.1 ± 0.2
$\Delta V_{ls}^{\ddagger}$	cm^3/mol	5.2 ± 2.0	3.9 ± 1.0
$\Delta V_{hs}^{\ddagger}$	cm^3/mol	−2.9 ± 1.5	−8.4 ± 2.0

[a] Reference 10.

We have no ready explanation for the observation that $\Delta V_{hs}^{\ddagger}$ is much more negative for II than for I except to note that the coordination spheres are considerably different and to suggest that detailed interpretation of such differences should await measurement of $\Delta V_{hs}^{\ddagger}$ values for a broader range of compounds and conditions. Further investigations into the volume profiles of these and related systems are in progress.

Acknowledgment. This research was supported by the National Science Foundation. H.A.G. was supported by a Fulbright Foundation Fellowship during his leave at UCSB.

Registry No. I, 18745-06-7; II, 94781-23-4.

---

(18) On leave from Department of Chemistry, University of New South Wales, Kensington, NSW, 2033 Australia.

Department of Chemistry and Quantum Institute
University of California
Santa Barbara, California 93106

John DiBenedetto
Valerie Arkle
Harold A. Goodwin[18]
Peter C. Ford*

Received September 24, 1984

Articles

Contribution from the Department of Chemistry,
Wayne State University, Detroit, Michigan 48202

Reactions of Coordinated β-Polyketonate Ligands. 1. Synthesis and Structure of Bis[1,7-diphenyl-1,3,4,5,7-heptanepentaonato(2−)]tetrakis(pyridine)dicobalt(II) Resulting from the Oxidation of Bis[1,7-diphenyl-1,3,5,7-heptanetetraonato(2−)]tetrakis(pyridine)dicobalt(II)

RICHARD L. LINTVEDT,* G. RANGER, and C. CECCARELLI

Received March 14, 1984

The binuclear Co(II) complex of 1,7-diphenyl-1,3,5,7-heptanetetraone, H_3DBAA, was prepared and characterized as $Co_2(HDBAA)_2(py)_4$. The Co(II) ions reside at the 1,3 and 5,7 enolate positions with the potential third coordination site in the center vacant. Crystallization of this compound from 10% by volume pyridine in benzene in the air resulted in oxidation of the 4-carbon of both ligands to carbonyls. The structure of the crystalline oxidation product bis[1,7-diphenyl-1,3,4,5,7-heptanepentaonato(2−)]tetrakis(pyridine)dicobalt(II)-4-pyridine, $Co_2(O{=}DBAA)_2(py)_4 \cdot 4py$ ($Co_2C_{78}H_{64}N_8O_{10}$), was determined by X-ray techniques. The crystal belongs to the triclinic space group $P1$ and has one molecule per unit cell. The lattice constants are a = 12.087 (7) Å, b = 12.435 (8) Å, c = 13.845 (9) Å, α = 67.71 (5)°, β = 70.76 (5)°, γ = 87.46 (5)°, and V = 1810 (2) $Å^3$.

Introduction

The β-polyketones are a homologous series of molecules that are potentially valuable ligands in the study of polynuclear metal complexes. They combine the general coordinating ability of the simplest member, the 1,3-diketones, with the capability to form homologous transition-metal complexes. Thus, they afford the unusual opportunity to investigate the physical and chemical significance of systematically increasing the number of metal ions per molecule in a controlled chemical environment. Our laboratory has expended a considerable effort during the past several years investigating the synthesis, structure, magnetism, and electrochemical properties of the binuclear metal complexes of the 1,3,5-triketonates, the second member of the homologous series. However, the ligating properties of the third series member, the 1,3,5,7-tetraketonates, are essentially unknown. Two brief reports from our laboratory[1,2] constitute the only published reports of 1,3,5,7-tetraketonate complexes, the latter of which describes the structure of a heterotrinuclear complex containing two UO_2^{2+} ions and one Ni(II). In addition, a paper describing the synthesis, structure, and electrochemistry of a series of heterotrinuclear tetraketonates, $(UO_2)_2M^{II}(DBAA)_2(py)_4$ where M^{II} = Zn, Cu, Ni, Co, Fe, and Mn, is now available.[3] This report includes the single-crystal structure determination of the M^{II} = Ni, Co, Fe, and Mn complexes. To our knowledge, this is the only information currently available.

An underlying reason for investigating polynuclear transition-metal complexes is the possibility that the presence of two or more metal ions may impart unusual chemical properties to these molecules. The polynuclear Co(II) complexes are of considerable interest in this regard inasmuch as they may exhibit both Co(III) and Co(I) redox chemistry and certain related mononuclear species have well-developed O_2 chemistry.[4] Our initial studies of binuclear Co(II) complexes dealt with structural-magnetic relationships[5] followed by a report of the use of binuclear

---

(1) Andrelczyk, B.; Lintvedt, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 8633.
(2) Lintvedt, R. L.; Schoenfelner, B. A.; Ceccarelli, C.; Glick, M. D. *Inorg. Chem.* **1982**, *21*, 2113.
(3) Lintvedt, R. L.; Schoenfelner, B. A.; Ceccarelli, C.; Glick, M. D. *Inorg. Chem.* **1984**, *23*, 2867.
(4) Basolo, F.; Hoffman, B. M.; Ibers, J. A. *Acc. Chem. Res.* **1975**, *8*, 384 and references therein.
(5) Kuszaj, J. M.; Tomlonovic, B. K.; Murtha, D. P.; Lintvedt, R. L.; Glick, M. D. *Inorg. Chem.* **1973**, *12*, 1297.