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Synthesis and Structure of Metal Complexes of Triaza Macrocycles with Three Pendant Pyridylmethyl Arms

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The preparation and characterization of iron(II) complexes of three new sexidentate N_6 ligands are reported. The three new ligands are constructed from 2,5,8-triazanonane, 1,4,7-triazacyclononane, or 1,5,9-triazacyclododecane by adding three pendant pyridylmethyl arms to each triamine. The X-ray structure of [Fe(tptcn)](ClO$_4$)$_2$, where tptcn is tris(2-pyridylmethyl)-1,4,7-triazacyclononane, has been determined by using Patterson methods, in conjunction with data measured on a four-circle diffractometer, to give discrepancy factors of $R_F = 0.041$ and $R_{wF} = 0.052$ for 1841 observed ($I > 2.58\sigma(I)$) reflections. The compound crystallizes in the trigonal space group *P*3 with three formula weights in a cell having the dimensions a = 16.978 (3) Å and c = 7.909 (3) Å. There are three crystallographically independent Fe(tptcn)$^{2+}$ cations; each cation has a C_3 axis perpendicular to the plane of the three pyridine nitrogen atoms as well as the plane of the three aliphatic nitrogen atoms of a tptcn ligand. All three cations have similar dimensions; the bond distances are appropriate for a low-spin Fe(II) complex, a description that is in agreement with the variable-temperature Mössbauer and magnetic susceptibility data that are obtained. The ClO$_4^-$ and SbF$_6^-$ salts of [Fe(tptan)]$^{2+}$ and [Fe(tptcd)]$^{2+}$ are high-spin Fe(II) compounds, where tptan is tris(2-pyridylmethyl)-2,5,8-triazanonane and tptcd is tris(2-pyridylmethyl)-1,4,7-triazacyclododecane. Electronic absorption spectral data are presented for the three iron(II) complexes in solution, as well as for the analogous cobalt(III) and nickel(II) complexes, to show that the [Fe(tptcn)]$^{2+}$ complex is close to the spin-crossover point. The interrelationships between the kinetics of reactions such as racemization and the possibility of converting from low spin to high spin, i.e. the existence of the spin-crossover phenomenon, are examined for the tptcn complex. ^{13}C NMR results are presented to show that [Fe(tptcn)]$^{2+}$ undergoes a relatively rapid racemization with a rate constant in excess of 150 s^{-1} at 90 °C. *P*3 is a polar space group, so the iron(II) cations in [Fe(tptcn)](ClO$_4$)$_2$ are one of an enantiomeric pair; i.e., the cations are optically active and resolved. The kinetics of racemization that develop after a crushed large single crystal is dissolved, monitored with a CD spectrometer, give a rate constant of $k = 2.7 \times 10^{-3}$ s^{-1} at 5 °C. It is suggested that the racemization takes place via an intramolecular twist mechanism and that such a mechanism is strongly favored by having a situation where the triplet excited state is close in energy to the singlet ground state of an iron(II) complex.

Introduction

Determination of the molecular mechanisms for intramolecular rearrangement reactions of chelate complexes is a long-standing problem. The proposed mechanisms for configurational racemization in tris chelate and multidentate complexes include the following: (a) the Bailar or trigonal twist about the real threefold molecular axis;[3] (b) the Rây–Dutt or rhombic twist about the imaginary threefold molecular axis;[4] (c) bond rupture with five-coordinated transition states having dangling ligands.[5]

From the results of kinetic studies on low-spin, tris chelate Fe(II) complexes, it has been concluded that the major path for racemization in solution is an intramolecular process and twist mechanisms have been proposed.[6] In the case where the central ion is an octahedral, low-spin d^6 system, it has been suggested that the racemization is synchronous with a spin-state isomerization.[9] An intermediate with triplet multiplicity and trigonal-prismatic geometry is shown to be energetically favorable. In a very recent paper these ideas are supported by the observation that low-spin complexes that are close to the spin-crossover point exhibit unusually rapid racemization kinetics.[10] Thus, in the case of [Fe(tpmbn)]$^{2+}$ (tpmbn = *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-2,4-*meso*-butanediamine) the racemization rate is 6 orders of magnitude faster than for [Fe(phen)$_3$]$^{2+}$.[11]

One way to favor a twist mechanism path is to use ligands which are designed in such a way that they, on coordination, give rise to a static twisted geometry. Results obtained in the last decades have clearly revealed that octahedral, trigonal-antiprismatic (TAP), trigonal-prismatic (TP), and intermediate geometries may be stabilized by the use of sexidentate ligands either with cage structure[12] or with an open trifurcated type of structure.[13] In a few cases efforts have been made to combine the properties of the relatively rigid and kinetically stable structural element of the macrocycles with the more flexible and kinetically labile open-chain ligands.[14] Wieghardt et al.[15] have described the binding properties of the ligand 1,4,7-triazacyclononane triacetate with several transition-metal ions and Hammershoi and Sargeson[16] have prepared the cobalt(III) complexes of tris(2-aminoethyl)-1,4,7-triazacyclononane.

In the present report we describe two new sexidentate ligand systems based on small N_3 macrocyclic rings with three pyridylmethyl dangling arms. In the case of the 9-membered ring system, a predominantly low-spin iron(II) complex is obtained, whereas with the 12-membered ring system, a high-spin complex is obtained. The pseudooctahedral geometry of the complexes is shown by the single-crystal X-ray structure of one of the complexes.

Experimental Section

Compound Preparation. 2,5,8-Triazanonane Trihydrochloride. Diethylenetriamine (108.5 mL, 1 mol) was neutralized with concentrated hydrochloric acid (250 mL) while the solution was stirred and cooled. Formaldehyde solution 35% (300 mL) was added, and the mixture was refluxed for 3 h. After evaporation of half the volume of solvent the mixture was cooled in ice for 1 h. The white product was filtered off and washed with ethanol. The crude product was recrystallized from a 1:2 mixture of water and ethanol. Yield: 12 g (5.6%).

Tris(2-pyridylmethyl)-2,5,8-triazanonane (tptan). 2,5,8-Triazanonane trihydrochloride (9.1 g, 0.038 mol) and 2-picolyl chloride hydrochloride (16.7 g, 0.114 mol) were dissolved in water (50 mL). During the following 4 days, a sodium hydroxide solution (80 mL, 4 M) was added with

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(1) University of Odense.
(2) University of Illinois.
(3) Bailar, J. C., Jr. *J. Inorg. Nucl. Chem.* **1985**, *8*, 165.
(4) Rây, P.; Dutt, N. K. *J. Indian Chem. Soc.* **1943**, *20*, 81.
(5) Gordon, J. G., II; Holm, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 5319.
(6) Basolo, F.; Hayes, J. C.; Neumann, H. M. *J. Am. Chem. Soc.* **1954**, *76*, 3807.
(7) VanMeter, F. M.; Neumann, H. M. *J. Am. Chem. Soc.* **1976**, *98*, 1388.
(8) Dowley, P.; Garbett, K.; Gillard, R. D. *Inorg. Chim. Acta* **1967**, *1*, 278.
(9) Purcell, K. F. *J. Am. Chem. Soc.* **1979**, *101*, 5147.
(10) McGarvey, J. J.; Heremann, K.; Toftlund, H., submitted for publication in *Inorg. Chem.*
(11) Lawrence, G. A.; Stranks, D. *Inorg. Chem.* **1978**, *17*, 1804.
(12) Comba, P.; Sargeson, A. M.; Engelhardt, L. M.; Harrowfield, J. Mac B.; White, A. H.; Horn, E.; Snow, M. R. *Inorg. Chem.* **1985**, *24*, 2325.
(13) Larsen, E.; LaMar, G. N.; Wagner, B. E.; Parkes, J. E.; Holm, R. H. *Inorg. Chem.* **1972**, *11*, 2652.
(14) Kaden, T. A. *Top. Curr. Chem.* **1984**, *121*, 157.
(15) Wieghardt, K.; Bossek, U.; Chaudhuri, P.; Herrmann, W.; Menke, B. C.; Weiss, J. *Inorg. Chem.* **1982**, *21*, 4308.
(16) Hammershoi, A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 3554.

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stirring to the cooled mixture in small enough portions so that the pH never exceeded 9. The mixture was evaporated under vacuum, and the residue was extracted with chloroform (4 × 50 mL). The chloroform extracts were dried over sodium sulfate and the chloroform was evaporated under vacuum. The residue was extracted with ligroin (4 × 50 mL). According to the ^{13}C NMR spectrum, the oil remaining after evaporation of the ligroin was practically pure. Yield: 6.8 g (50%).

1,4,7-Triazacyclononane trihydrobromide was prepared from the tritosylate of diethylenetriamine and the ditosylate of 1,2-ethanediol according to Richman and Atkins.[17]

Tris(2-pyridylmethyl)-1,4,7-triazacyclononane (tptcn) was prepared in a manner analogous to that used for the tptan ligand except that the chloroform extraction turned out not to be necessary because the ligand precipitated before all the sodium hydroxide was added.

Tris(2-pyridylmethyl)-1,5,9-triazacyclododecane (tptcd) was prepared in a manner analogous to that of the ligand tptan.

[Fe(tptan)](ClO$_4$)$_2$·H$_2$O. This preparation was performed in an inert-atmosphere glovebox due to the air sensitivity of the product. Iron(II) perchlorate hexahydrate (0.36 g, 1 mmol) was dissolved in a 1:1 water–methanol mixture (10 mL). The solution was heated to 50 °C, and tptan (0.4 g, 1 mmol) was added with stirring. Before the mixture was cooled to room temperature, solid sodium perchlorate (1 g) was added. The yellow-green product was filtered off, washed, and dried under vacuum. Yield: 0.24 g (35%). Anal. Calcd for $[FeC_{24}H_{32}N_6](ClO_4)_2 \cdot H_2O$: C, 42.56; H, 5.06; N, 12.41; Cl, 10.47. Found: C, 42.00; H, 4.95; N, 12.01; Cl, 10.52.

[Fe(tptcn)](ClO$_4$)$_2$ was prepared in an analogous manner but is not air-sensitive. Anal. Calcd for $[FeC_{24}H_{30}N_6](ClO_4)_2$: C, 43.86; H, 4.60; N, 12.79; Cl, 10.79. Found: C, 43.51; H, 4.53; N, 12.84; Cl, 10.69.

[Fe(tptcd)](ClO$_4$)$_2$·H$_2$O was prepared analogously. Yield: 85 mg (26%).

[Co(tptan)](ClO$_4$)$_3$. *trans*-$[Co(py)_4Cl_2]Cl \cdot 6H_2O$ (0.59 g, 1 mmol) was dissolved in methanol (8 mL), and a methanolic solution of tptan (0.4 g, 1 mmol in 2 mL) was added. The mixture was heated to 50 °C for 5 min and then evaporated to dryness in vacuum. The residue was dissolved in water, and the red complex was precipitated with sodium perchlorate (2 mL of a saturated solution). Yield: 0.4 g (53%). Separation on a Sephadex C-25 column gave two bands. The first band (30%) was assumed to be the meridional isomer and the other band, the facial isomer.

[Co(tptcn)](ClO$_4$)$_3$ was prepared analogously. Yield: 0.5 g (66%).

[Co(tptcd)](ClO$_4$)$_3$ was prepared analogously. Yield: 0.33 g (42%).

[Ni(tptan)](ClO$_4$)$_2$. Nickel(II) perchlorate (0.183 g, 0.5 mmol) was dissolved in 10 mL of 50 °C hot water, and a solution of tptan (0.2 g, 0.5 mmol) dissolved in methanol (5 mL) was added with stirring. On cooling to room temperature, violet crystals precipitated. The product was filtered off, washed, and dried in air. Yield: 0.2 g (60%).

[Ni(tptcn)](ClO$_4$)$_2$ was prepared analogously. Yield: 0.25 g (75%).

[Ni(tptcd)](ClO$_4$)$_2$ was prepared analogously. Yield: 0.2 g (52%).

CD Measurement. A crushed single crystal of [Fe(tptcn)](ClO$_4$)$_2$ was quickly dissolved in an ice-cold 1:1 mixture of acetone and water and transferred to an isolated precooled cell holder in the cell house of the machine. Repeat scans were run for 15 min.

Instruments. A Cary 219 spectrophotometer was used for spectrophotometric measurements in the visible and near-UV region. Circular dichroism spectra were measured with a Jasco J40A dichrograph. Proton-decoupled 15.03-MHz ^{13}C NMR spectra were recorded on a JEOL FX-60 NMR spectrometer. Magnetic susceptibilities were measured by using a VTS-50 SQUID susceptometer (SHE Corp). A magnetic field of 10 kG was used. ^{57}Fe Mössbauer data were collected on a previously described instrument.[18]

Crystal Measurements and Data Collection. The translucent red crystal of [Fe(tptcn)](ClO$_4$)$_2$ used for data collection was a small fragment from a large twinned crystal. The sample sharply extinguished plane-polarized light despite the poorly defined faces and numerous internal flaws. The crystal was bound by the following faces: (−2,1,0), (010), (0,−1,0), (100), (−3,1,1), (111), (−1,−1,−1), (011), and (001). Distances from the crystal center to these estimated facial boundaries were 0.08, 0.12, 0.12, 0.13, 0.14, 0.20, 0.20, 0.22, and 0.28 mm, respectively. The crystal was mounted with epoxy to a thin glass fiber with the (−1,0,−1) scattering planes roughly normal to the spindle axis. The unit cell parameters listed in Table I were obtained by a least-squares fit to the automatically centered settings for 25 reflections. Details of the data collection may also be found in Table I. No evidence for crystal decomposition was noted. The data were corrected for Lorentz, polarization, and anomalous dispersion effects. A numerical absorption correction was also applied; maximum and minimum transmission factors were 0.852 and 0.805. The Laue group could not be photographically confirmed without remounting the sample, so a triclinic data set was measured. These data were internally consistent with a threefold symmetry axis.

Table I. Experimental and Crystal Data for the X-ray Structure of [Fe(tptcn)](ClO$_4$)$_2$

Crystal Parameters

cryst stat: trigonal
$a = 16.978$ (3) Å
$b = a$
$c = 7.909$ (3) Å
$V = 1974$ (1) Å^3
fw: 657.29
ρ(calcd) = 1.659 g cm^{-3}

space group: $P3$
$\alpha = 90°$
$\beta = \alpha$
$\gamma = 120°$
$Z = 3$
$\mu = 8.36$ cm^{-1}

Data Measurement

diffractometer: Enraf-Nonius CAD4 automated κ-axis
radiation: graphite monochromatized Mo Kα ($\lambda = 0.71073$ Å)
2θ limits: $2.0° < 2\theta < 46.0°$
ω/θ scan range: $1.50[1.00 + 0.35 \tan \theta]°$
no. of unique data measd: 2009 ($\pm h, \pm k, -l$)
data used: $I > 2.58\sigma(I)$; 1841 reflcns
transmission factor limits: 0.805–0.852
internal consistency: $R_i = 0.026$
$R_F{}^a = 0.041$
$R_{wF}{}^a = 0.052$

[a] $R_F = \sum|F_o - |F_c||/\sum F_o$; $R_{wF} = \{\sum w(F_o - |F_c|)^2/\sum wF_o{}^2\}^{1/2}$.

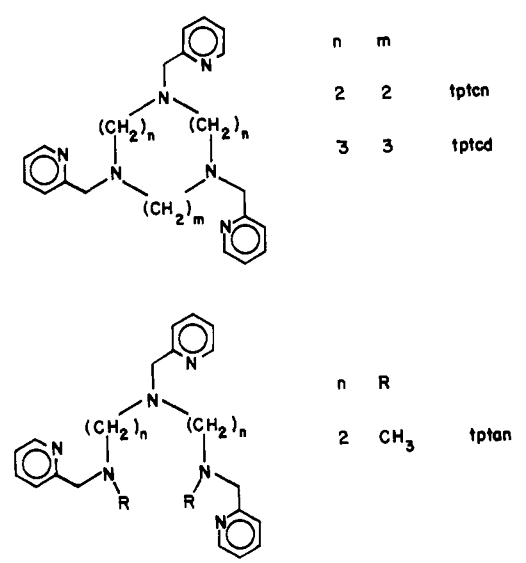

Figure 1. General structural drawing for the three ligands used in this study.

Structure Solution and Refinement. The structure of [Fe(tptcn)](ClO$_4$)$_2$ was solved by Patterson methods; correct positions for the three iron atoms were deduced from a sharpened Patterson map. A weighted difference Fourier summation revealed positions for the two chlorine and six nitrogen atoms, and subsequent least squares-difference Fourier calculations gave positions for the remaining non-hydrogen atoms. In the final cycle of least squares, a group isotropic thermal parameter was varied for the hydrogen atoms, which were fixed in calculated positions, independent isotropic thermal coefficients were refined for the carbon atoms, and anisotropic thermal coefficients were refined for the remaining atoms. Successful convergence was indicated by the maximum shift/error for the last cycle. Refinement of the alternate enantiomer converged with residuals of $R_F = 0.044$ and $R_{wF} = 0.057$, indicating the original choice was correct. The anisotropic thermal coefficients for some of the perchlorate oxygen atoms were abnormally high, but no discrete disorder pattern was evident. The six peaks with density greater than background (+0.67 > e/Å^3 > −0.32) in the final difference Fourier map were in the vicinity of the two perchlorate anions. There were no significant systematic errors among the final observed and calculated structure factors.

The final positional parameters for all refined atoms can be found in Table II. Listings of the thermal parameters, "idealized" hydrogen atom

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(17) Richman, J. E.; Atkins, T. J. *J. Am. Chem.* **1974**, *96*, 2268.
(18) Cohn, M. J.; Timken, M. D.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1984**, *106*, 6683.

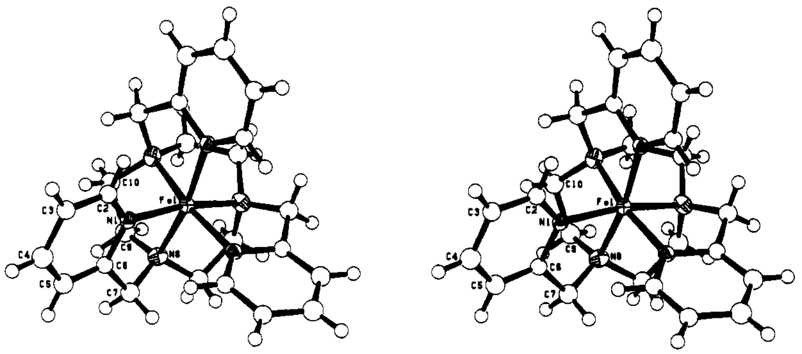

Figure 2. ORTEP stereoview of one of the three crystallographically inequivalent catrions in [Fe(tptcn)]$(ClO_4)_2$. The viewing direction is approximately down the crystallographic C_3 axis of the cation.

positions, and observed and calculated structure factors are available as supplementary material.

Results and Discussion

Three new sexidentate ligands, where an aliphatic triamine backbone has been combined with three 2-pyridylmethyl pendant arms (Figure 1), have been prepared by using the substitution procedure described by Toftlund and Yde-Anderson.[19] One ligand is a branched open-chain system (tptan) based on 2,5,8-triazanonane. The other two ligands are the symmetric ($n = m$) systems based on 1,4,7-triazacyclononane (n = 2) (tptcn) and 1,5,9-triazacyclododecane (n = 3) (tptcd).

The iron(II), cobalt(III), and nickel(II) complexes have been prepared by using $[Fe(H_2O)_6](ClO_4)_2$, *trans*-$[Co(py)_4Cl_2]Cl\cdot 6H_2O$, and $[Ni(H_2O)_6](ClO_4)_2$, respectively, as starting materials. The complexes have been characterized through their analytical data and electronic spectra and in the case of the iron complexes also Mössbauer spectra and magnetic susceptibility data.

In our design of these new ligand systems the goal has been to find new iron(II) spin-crossover systems. The rationale behind this expectation is the fact that the tris((2-pyridylmethyl)amine)iron(II), i.e. $[Fe(pic)_3]Cl_2\cdot 2H_2O$, is a spin-crossover system. However, it is too labile to investigate in solution.[20] By linking the three nitrogen atoms together either in a chain or in a ring it was our hope to construct new spin-crossover systems with multidentate ligands, which might be stable in solution. That we did not quite succeed (vide infra) in this aim is not surprising. It must be remembered that it is necessary to fine tune the ligand field strength to within 2–3% if we are to observe the spin-crossover phenomenon. We have changed two factors in going from (2-pyridylmethyl)amine to our ligands. First, by substitution of all hydrogen atoms on the amine groups, we have lost any possibility for hydrogen-bonding stabilization of our system. On the other hand, we have obtained a stabilization through the introduction of a new chelate ring in the final complexes. In the case of tptcn, where three new five-membered chelate rings are introduced compared to the tris(picolyamine) complexes, the net stabiization is high enough to give a predominantly low-spin iron(II) complex, despite the fact that the whole system is twisted 5° more along a trigonal path than the corresponding *fac*-$[Fe(pic)_3]Cl_2\cdot 2H_2O$ system.[21] It is interesting that if just one of the three chelate rings coming from the macrocycle is cleaved, the resulting iron(II) $[Fe(tptan)]X_2$ complexes are high spin. This observation suggests that the macrocyclic effect might be important for the stabilization of the $[Fe(tptcn)]^{2+}$ ion as low spin. If the macrocyclic effect is retained but all three new chelate rings are six-membered, i.e. [Fe(tptcd)], we again obtain a predominantly high-spin complex, suggesting that combinations where n and m (Figure 1) are different might lead to the goal.

Table II. Positional Parameters for $[Fe(tptcn)](ClO_4)_2$

	x/a	y/b	z/c
Fe(1)[a]	0.0	0.0	0.0
Fe(2)[a]	0.03333	0.66667	−0.0142 (3)
Fe(3)[a]	0.66667	0.33333	−0.1823 (3)
Cl(A)	0.6684 (1)	0.7111 (1)	0.5500 (4)
Cl(B)	0.6671 (1)	0.0329 (2)	0.2392 (3)
O(1)	0.6648 (10)	0.6280 (6)	0.553 (2)
O(2)	0.671 (1)	0.738 (1)	0.718 (2)
O(3)	0.7501 (7)	0.7797 (10)	0.505 (2)
O(4)	0.5959 (7)	0.7086 (8)	0.471 (2)
O(5)	0.615 (1)	0.055 (2)	0.323 (2)
O(6)	0.6594 (8)	−0.0506 (6)	0.271 (2)
O(7)	0.6776 (10)	0.0570 (8)	0.074 (1)
O(8)	0.748 (1)	0.0905 (9)	0.318 (2)
N(1)	−0.0823 (4)	0.0272 (4)	−0.1335 (8)
N(8)	0.0052 (4)	0.0955 (4)	0.1542 (8)
N(11)	0.3430 (4)	0.5726 (4)	−0.1455 (8)
N(18)	0.2588 (4)	0.5623 (4)	0.1415 (8)
N(21)	0.7701 (4)	0.3419 (4)	−0.0525 (8)
N(28)	0.7657 (4)	0.4195 (4)	−0.3376 (8)
C(2)	−0.1379 (5)	−0.0189 (5)	−0.2588 (10)
C(3)	−0.1883 (5)	0.0091 (5)	−0.347 (1)
C(4)	−0.1819 (6)	0.0908 (5)	−0.301 (1)
C(5)	−0.1258 (5)	0.1389 (5)	−0.169 (1)
C(6)	−0.0773 (5)	0.1074 (5)	−0.0868 (9)
C(7)	−0.0093 (5)	0.1594 (5)	0.050 (1)
C(9)	−0.0670 (5)	0.0512 (6)	0.288 (1)
C(10)	−0.1392 (6)	−0.0428 (5)	0.232 (1)
C(12)	0.4013 (5)	0.5844 (5)	−0.2712 (9)
C(13)	0.4021 (5)	0.5131 (5)	−0.353 (1)
C(14)	0.3391 (5)	0.4258 (5)	−0.304 (1)
C(15)	0.2793 (5)	0.4123 (5)	−0.1750 (10)
C(16)	0.2824 (5)	0.4868 (5)	−0.0984 (9)
C(17)	0.2166 (5)	0.4784 (5)	0.0373 (10)
C(19)	0.3199 (5)	0.5568 (5)	0.2742 (10)
C(20)	0.4181 (5)	0.6081 (5)	0.219 (1)
C(22)	0.7691 (5)	0.2872 (5)	0.0732 (9)
C(23)	0.8484 (5)	0.3005 (5)	0.1497 (10)
C(24)	0.9310 (6)	0.3693 (5)	0.094 (1)
C(25)	0.9325 (5)	0.4252 (5)	−0.033 (1)
C(26)	0.8530 (5)	0.4111 (5)	−0.1027 (9)
C(27)	0.8481 (5)	0.4713 (5)	−0.2332 (10)
C(29)	0.7820 (5)	0.3662 (5)	−0.470 (1)
C(30)	0.7449 (5)	0.2674 (5)	−0.4166 (10)

[a] Atom constrained to lie on a threefold symmetry axis.

Molecular and Crystal Structure of $[Fe(tptcn)](ClO_4)_2$. This complex crystallizes in the trigonal space group $P3$. There are three $[Fe(tptcn)]^{2+}$ cations in the unit cell; each cation has a C_3 axis perpendicular to the plane of the three pyridine nitrogen atoms as well as the plane of the three aliphatic nitrogen atoms of a tptcn ligand. Figure 2 shows a stereoview of one of the three cations, viewed approximately down the C_3 axis. All three crystallographically different cations have very similar dimensions, and, as a consequence, selected bond distances and angles for the average cation are given in Table III. Dimensions for the three independent cations are available in the supplementary material.

It is clear from Figure 2 that the tptcn molecule acts as a sexidentate ligand. The ligand molecule coordinates to the iron(II) through six nitrogen atoms, forming a pseudooctahedral first-

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(19) Toftlund, H.; Yde-Andersen, S. *Acta Chem. Scand., Ser. A* **1981**, *A35*, 575.

(20) Chum, H. L.; Vanin, J. A.; Holanda, M. I. D. *Inorg. Chem.* **1982**, *21*, 1146.

(21) Sinn, E. *J. Am. Chem. Soc.* **1978**, *100*, 8080.

Table III. Weighted Mean Bond Distances (Å) and Angles (deg) for the Average $[Fe(tptcn)]^{2+}$ Cation[a]

	Distances		
Fe–N(1)	1.979 (6)	Fe–N(8)	2.001 (6)
N(1)–C(2)	1.342 (9)	C(2)–C(3)	1.37 (1)
C(3)–C(4)	1.38 (1)	C(4)–C(5)	1.38 (1)
N(1)–C(6)	1.362 (9)	C(5)–C(6)	1.36 (1)
N(8)–C(7)	1.479 (9)	C(6)–C(7)	1.50 (1)
N(8)–C(9)	1.51 (1)	C(9)–C(10)	1.52 (1)
N(8)–C(10)	1.490 (10)		
	Angles		
N(1)–Fe–N(1)[a]	94.8 (2)	N(1)–Fe–N(8)	83.1 (2)
N(1)–Fe–N(8)[a]	96.0 (2)	N(1)–Fe–N(8)[a]	169.0 (2)
N(8)–Fe–N(8)[a]	86.4 (3)	Fe–N(1)–(2)	129.9 (5)
Fe–N(1)–C(6)	113.5 (5)	C(2)–N(1)–C(6)	117.5 (6)
Fe–N(8)–C(7)	107.2 (5)	Fe–N(8)–C(9)	109.3 (4)
Fe–N(8)–C(10)[a]	106.1 (5)	C(7)–N(8)–C(9)	110.4 (5)
C(7)–N(8)–C(10)[a]	112.9 (6)	C(9)–N(8)–C(10)[a]	110.7 (6)
N(1)–C(2)–C(3)	123.0 (7)	C(2)–C(3)–C(4)	118.6 (7)
C(3)–C(4)–C(5)	118.9 (7)	C(4)–C(5)–C(6)	119.9 (7)
N(1)–C(6)–C(5)	121.8 (7)	N(1)–C(6)–C(7)	114.8 (6)
C(5)–C(6)–C(7)	123.6 (6)	N(8)–C(7)–C(6)	109.5 (6)
N(8)–C(9)–C(10)	111.1 (6)	C(9)–C(10)–N(8)[a]	108.8 (6)

[a] Atom in equivalent position generated by a threefold symmetry axis.

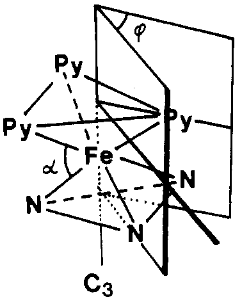

Figure 3. Definition of two structural parameters: the twist angle ϕ and the chelate bite angle α.

coordination sphere. The weighted mean Fe–N(py) and Fe–N(aliphatic) distances are 1.979 (6) and 2.001 (6) Å, respectively, for the $[Fe(tptcn)]^{2+}$ cation pictured in Figure 2. Since $[Fe(tptcn)](ClO_4)_2$ is a low-spin complex (vide infra), it is appropriate to compare these two distances with the corresponding distances in low-spin $[Fe(pic)_3]Cl_2{\cdot}2H_2O$, where the average distances are Fe–N(py) = 1.986 Å and Fe–N(NH_2) = 2.026 Å.[21] The distances are similar, except the Fe–N(aliphatic) distance in the tptcn complex is ~0.03 Å shorter than the Fe–N(NH_2) distance in the picolylamine complex. Boeyens et al.[22] very recently reported the structure of low-spin $[Fe([9]aneN_3)_2]Cl_2{\cdot}4H_2O$, where the tridentate ligand is 1,4,7-triazacyclononane. They found an average Fe–N distance of 2.03 Å, which again exceeds by ~0.03 Å the Fe–N(aliphatic) distance to the 1,4,7-triazacyclononane moiety in the tptcn complex. Angles and distances within the triazacyclononane rings of the tptcn and $[9]aneN_3$ complexes are very close. In both cases, due to the puckering of the coordinated triazacyclonane ring, the ethylene carbon atoms fall into two groups of three equivalent atoms. The three chelate rings of the coordinated triazacyclononane are not planar. In the tptcn complex the torsion angles in the three N–C–C–N fragments of this macrocyclic moiety vary from 25.7 to 29.2°, which is to be compared to torsion angles of 19.3 ± 0.1° in the free ligand.

It was anticipated that fusing six five-membered chelate rings in the coordination sphere of the tptcn complex would result in a rather inflexible molecule. The ligand tptcn is expected to favor a trigonal-prismatic structure. However, if it is ligated to a metal ion such as low-spin iron(II), which has a large ligand-field preference for an octahedral geometry, then a structure that is dictated by a compromise between ligand strain and ligand field stabilization effects would be expected. In Figure 3 two structural parameters are defined: the twist angle ϕ and the chelate bite angle α. The twist angle ϕ can vary from zero for a trigonal-prismatic complex to 60° for an octahedral complex. In the case of $[Fe(tptcn)](ClO_4)_2$, $\phi = 48.9\ (3)°$ and $\alpha = 83.1\ (2)°$. These values can be compared with the corresponding values for several other iron complexes with hexadentate ligands as summarized in Table IV.

Table IV. Structural Parameters

complex	α, deg	ϕ, deg	ref
octahedron	90	60	
trigonal prism	81.8	0	
$[Fe(tptcn)](ClO_4)_2$	83.1	48.9	this work
$[Fe^{II}di(amH)sar](NO_3)_4{\cdot}H_2O$	81.2	28.6	10
$[Fe(tach)(py)_3](ClO_4)_2$		45	
$[Fe(tren)(py)_3](ClO_4)_2$		54	11
$[Fe(tcn)_2]Br_2{\cdot}H_2O$		58	22
fac-$[Fe(pic)_3]_2$	82.3	53.7	16
$[Fe^{III}tcnta]$		26.6	13

A stereo packing diagram for $[Fe(tptcn)](ClO_4)_2$ is shown in Figure 4, which is available as the supplementary material. There are no strong intermolecular contacts or hydrogen bonds, but four hydrogen atoms of the ligand are directed toward perchlorate oxygen atoms within the distance range 2.52–2.62 Å. As an aside, it is interesting to note that $[Fe(tptcn)](ClO_4)_2$ is isostructural with the iron(III) complex $[Fe([9]aneN_3)_2]Cl_3{\cdot}5H_2O$.[22]

Magnetic Properties. In the case of the non macrocyclic ligand complex $[Fe(tptan)](ClO_4)_2$ a rather constant effective magnetic moment (μ_{eff}) of 4.5–4.7 μ_B was observed in the temperature range 106–409 K, and nearly the same values were found for the corresponding SbF_6^- salt. These tptan complexes are high-spin complexes. Measurements of the magnetic susceptibilities of $[Fe(tptcn)](ClO_4)_2$ in the temperature range 303–406 K support the expectations that this complex is predominantly low-spin. The magnetic moment varies from 1.20 to 1.26 μ_B, which in large part must be ascribed to temperature-independent paramagnetism.

The magnetic susceptibility of $[Fe(tptcd)](ClO_4)_2$ has been measured in the range 107–303 K, where the magnetic moment was found to increase from 3.71 to 4.13 μ_B; however, the corresponding hexafluoroantimonate salt showed a nearly constant magnetic moment of 4.9 μ_B through the whole temperature range of 20–310 K. Thus, this complex is predominantly or totally high spin, depending on the size of the anion.

^{57}Fe Mössbauer Spectra. The Mössbauer spectra of $[Fe(tptan)](ClO_4)_2$ has been recorded at 4.2, 120, and 265 K. At all three temperatures the spectrum is dominated by a typical high-spin signal with $\delta = 1.06–0.90$ mm s^{-1} and $\Delta E_Q = 3.15–2.8$ mm s^{-1}. A weak low-spin signal was observed as well, which increased in intensity from 14% of the total spectral area at 4.2 K to 30% at 265 K. This is quite the opposite behavior expected for a spin-crossover complex. We would suggest that this sample is a mixture of two isomeric forms of the complex (*fac* and *mer*?). In the case of $[Fe(tpan)](SbF_6)_2$ this low-spin signal was hardly discernible at 120 K.

The Mössbauer spectrum of $[Fe(tptcn)](ClO_4)_2$ was recorded at 100 and 340 K. In both cases typical low-spin iron(II) signals centered at $\delta = 0.293$ and 0.349 mm s^{-1}, respectively, were observed. The quadrupole splitting (ΔE_Q) was found in both cases to be very small, 0.168 and 0.176 mm s^{-1}, respectively, indicating that the ligand field has a symmetry that deviates very little from cubic symmetry. This is in agreement with the X-ray structural results.

In the case of the $[Fe(tptcd)]^{2+}$ cation only the SbF_6^- salt was examined with the Mössbauer technique. At 120 K two high-spin quadrupole doublets with the intensity ratio 2:1 were observed: $\delta_1 = 1.021$, $\delta_2 = 1.074$ mm s^{-1} and $\Delta E_{Q1} = 2.521$, $\Delta E_{Q2} = 1.959$ mm s^{-1}. It is likely that these two signals arise from cations that are at the inequivalent crystallographic sites shown in Figure 4.

Electronic Absorption Spectra. The band maxima in the electronic absorption spectra of the iron(II) complexes in the

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[22] Boeyens, J. C.; Forbes, A. G. S.; Hancock, R. D.; Wieghardt, K. *Inorg. Chem.* **1985**, *24*, 2926–31.

Table V. Electronic Spectra

compd	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	ref
$[Fe(tptan)]^{2+}$ [a]	369 (1130)	*b*
$[Fe(tptcn)]^{2+}$	434 (12 230)	*b*
$[Fe(tptcd)]^{2+}$	362 (1120)	*b*
fac-$[Fe(pic)_3]^{2+}$	432 (3210)	15
$[Co(tptan)]^{3+}$	482, 350 sh	*b*
$[Co(tptcn)]^{3+}$	473 (292), 347 (255)	*b*
$[Co(tptcd)]^{3+}$	496, 350 sh	*b*
fac-$[Co(pic)_3]^{3+}$	462, 350 sh	*b*
$[Co(taetacn)]^{3+}$	480 (242), 347 (198)	14

[a] Solvent: water. [b] This work.

visible–ultraviolet region are shown in Table IV. Only in the case of $[Fe(tptcn)]^{2+}$ is the intense metal-to-ligand charge-transfer band typical for low-spin iron(II) complexes seen. Compared to the systems containing sexidentate ligands of the tetrakis(2-pyridylmethyl)ethylenediamine (tpen) type,[19] the band in the tptcn complex is redshifted 9 nm but the shape of the band is very similar. The two other complexes exhibit spectral properties very similar to what have been found for the high-spin tpen type complexes.[19]

Table IV also contains the maxima of the first ligand field bands $^1T_{1g} \leftarrow {}^1A_{1g}$ of the isoelectronic cobalt(III) complexes. These bands can be used to judge the relative ligand field strengths of the ligands as pointed out by Toftlund et al.[19] As a rule the calculated Δ values are 1.28 times the Δ_{ls} value for the corresponding iron(II) complex. The critical range, leading to spin-crossover behavior, is found to be $17.0 \times 10^3 < \Delta_{ls}(Fe(II)) < 17.6 \times 10^3$ cm^{-1}. As Δ for $[Co(tptcn)]^{3+}$ is found to be 22.16×10^3 cm^{-1}, it is seen that the predicted $\Delta_{ls}(Fe(II))$ is 17.3×10^3 cm^{-1}, which ought to give a crossover complex. However, the energy of the second ligand field band in $[Co(tptcn)]^{3+}$ (28.88×10^3 cm^{-1}) is red-shifted about 1.4×10^3 cm^{-1} relative to the $[Co(tpen)]^{3+}$ complexes, suggesting a significant reduction in the interelectronic repulsion parameter B corresponding to a decrease in the spin-pairing energy P. These changes we ascribe to a higher covalency in the macrocyclic complex system. Thus, there is a slight tendency to shorter Fe–N distances of the aliphatic N atoms in $[Fe(tptcn)](ClO_4)_2$ as compared to other picolylamine systems. Furthermore, it is known that aliphatic macrocyclic rings such as cyclam stabilize the low-spin state in Ni(II), and the 1,4,7-triazacyclononane ligand is reported to give a low-spin bis complex with Fe(III)[23] and Fe(II).[22]

It is interesting that in the *fac*-$[Co(pic)_3]^{3+}$ system the ligand field strength is greater than in $[Co(tpten)]^{3+}$, whereas the pure aliphatic system $[Co(tpetaen)]^{2+}$ exhibits a smaller ligand field.[16] The intensities of the ligand field bands in $[Co(tptcn)]^{3+}$ are three times the value normally seen for luteo complexes. This fact might be a consequence of the trigonal distortion of the chromophore.

The Δ values for $[Co(tptan)]^{3+}$ and $[Co(tptcd)]^{3+}$ are both so low that high-spin behavior is predicted for the corresponding iron(II) complexes, in agreement with the observations.

The positions of the ligand field transitions in the Ni(II) complexes of the present ligands are shown in Table V. The same trend as discussed for the iron(II) and cobalt(III) complexes is also seen.

Racemization Kinetics. From a chemical point of view the interest in the spin-state interconversion dynamics of iron(II) complexes derives from the question of how it may influence the kinetics of reactions such as electron transfer, hydrolysis, and racemization. Because the iron(II) complex of tptcn is expected to be close to the spin-crossover point, we have examined the dynamics of the complex in DMF with ^{13}C NMR spectroscopy. At room temperature there is no indication of line broadening or chemical exchange. The number of lines clearly shows that the complex has the same chiral, near-octahedral structure as shown in the crystal structure. In this configuration the macrocyclononane ring is puckered in such a way that the two carbon atoms in each ethylene ring are nonequivalent. However, in the hypothetical trigonal-prismatic structure these carbon atoms are equivalent. When the temperature of the solution is raised to 87 °C some of the lines move a few ppm but they are still narrow except the two lines from the macrocyclononane ring, which collapse in a way typical for chemical exchange on the ^{13}C NMR time scale. The two sets of ethylene carbon atoms are separated by 30 Hz at room temperature. When they collapse at about 90 °C the rate constant must be of the order of magnitude of 150 s^{-1} at this temperature, which is several orders of magnitude faster than the racemization rate for typical low-spin iron(II) complexes such as $[Fe(phen)_3]^{2+}$.[11]

Because of the rapid racemization of $[Fe(tptcn)]^{2+}$ an optical resolution using the normally available procedures is not possible. However, as shown by the crystal structure of $[Fe(tptcn)](ClO_4)_2$, this is one of the rare cases where a spontaneous resolution takes place. In order at the same time to measure the CD spectrum and to obtain some kinetic data for the racemization, we performed CD measurements in cooled solutions of crushed large single crystals of $[Fe(tptcn)](ClO_4)_2$. A linear plot of the logarithm of the CD deflection was obtained for 4 half-lives in an experiment run at 5 °C. The rate constant was found to be $k = 2.7\ 10^{-3}\ s^{-1}$, which still is a surprisingly high value. From this experiment and the ^{13}C NMR experiment discussed above, we obtained an estimate of the activation energy for the racemization reaction of 110 kJ/mol. This is quite a high value for such a fast reaction; however, a high value is expected if the mechanism requires a concerted movement of many atoms as in a twist mechanism.

For tris bidentate systems the two alternative twist mechanisms are not easily distinguished. However, in this case the steric strain in the cyclononane ring will strongly favor the Bailar twist mechanism.

Purcell and Zapata[24] argue that if, as in the present case, the resonances initially collapse and subsequently experience the contact shift, then $k_{ex} \gtrsim k_{spin}$. However, as we shall show below, this is not true in general and probably the situation $k_{spin} >> k_{ex}$ is much more common.

If we assume that the enantiomerization is a two-step reaction involving the spin change, then we have the following scheme:

$$\Delta(^1A_1) \xrightleftharpoons[k_{-1}]{k_1} \Delta(^5T_2) \xrightleftharpoons[k_{-2}]{k_2} \Lambda(^5T_2) \xrightleftharpoons[k_1]{k_{-1}} \Lambda(^1A_1)$$

The racemization rate constant (k_{ex} for $\Delta \rightarrow \Lambda$) derived with the assumption that the concentration of high-spin species are in the steady state is

$$k_{ex} = \frac{k_2(k_1 - k_{-1}K^{-1}{}_{eq})}{k_{-1} + k_2}$$

where $K_{eq} = [HS]/[LS] = k_1/k_{-1}$. For $k_1 >> k_{-1}$, the expression reduces to $k_{ex} = k_2K_{eq}$, so it is the spin-crossover equilibrium constant and not the spin-crossover interconversion rate constants k_1 and k_{-1} that determine the exchange rate. If k_2 is sufficiently large, even a very small K_{eq} will lead to a large value for k_{ex} and that, we suggest, is the common case. We shall even revive an old proposal regarding racemization in cobalt(III) complexes.[25] Although the paramagnetic states in most pseudooctahedral Co(III) complexes are energetically well above the ground state, it is not excluded that a small fraction can be populated at temperatures above room temperature and in that way give rise to a rapid racemization rate.

Thus, we suggest that the racemization takes place via an intramolecular twist mechanism and that such a mechanism is strongly favored in a low-spin iron(II) complex by having a ligand field state of triplet spin multiplicity close to the ground state. As shown by Purcell[24] and ourseleves[10] spin change and racemization might very well take place along the same trigonal twist

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(23) Wieghardt, K.; Tolksdorf, I.; Herrmann, W. *Inorg. Chem.* **1985**, *24*, 1230.

(24) Purcell, K. F.; Zapata, J. P. *J. Chem. Soc., Chem. Commun.* **1978**, 497.

(25) Davies, N. R. *Rev. Pure Appl. Chem.* **1954**, *4*, 66.

2818 *Inorg. Chem.* **1986**, *25*, 2818-2824

reaction coordinate. The rate of the spin-change reaction has in all cases which have been investigated found to be of the order of magnitude of 10^6–10^7 s^{-1}, so the rate of the racemization reaction will not be restricted by any spin-change bottleneck.

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Supplementary Material Available: Listings of thermal parameters, hydrogen atom positions, and bond distances and angles for [Fe(tptcn)](ClO$_4$)$_2$ and Figure 4, a stereoview of the unit cell (4 pages). Ordering information is given on any current masthead page.

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Magnetic Exchange Interactions in Some Novel μ-Azido-Bridged Copper(II) Dimers. Crystal Structures of [$L_2Cu_2(\mu\text{-}N_3)(N_3)_2$]($ClO_4$)·$H_2O$, $LCu(N_3)_2$, [$L_2Cu_2(\mu\text{-}N_3)_2(ClO_4)_2$], and $L'Cu(N_3)_2$ (L = *N,N′,N″*-Trimethyl-1,4,7-triazacyclononane and L′ = 1,4,7-Triazacyclononane)

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The reaction of Cu(ClO$_4$)$_2$·6H$_2$O in aqueous solution with *N,N′,N″*-trimethyl-1,4,7-triazacyclononane (L = C$_9$H$_{21}$N$_3$) and sodium azide yields black crystals of [L$_2$Cu$_2$(μ-N$_3$)(N$_3$)$_2$](ClO$_4$)·H$_2$O (**1**) and [L$_2$Cu$_2$(μ-N$_3$)$_2$(ClO$_4$)$_2$] (**3**). If Cu(CH$_3$CO$_2$)$_2$ is used as starting material, neutral complexes LCu(N$_3$)$_2$ (**2**) and L′Cu(N$_3$)$_2$ (**4**) could be isolated as crystalline solids, where L′ represents 1,4,7-triazacyclononane (C$_6$H$_{15}$N$_3$). The crystal structures of **1**–**4** have been determined by X-ray crystallography. **1** crystallizes in the monoclinic system, space group $C2/c$, with a = 29.64 (1) Å, b = 14.756 (5) Å, c = 15.700 (4) Å, β = 117.42 (2)°, and Z = 8. The structure was refined to a final R value of 0.053 for 5193 unique reflections. The structure consists of binuclear [L$_2$Cu$_2$(μ-N$_3$)(N$_3$)$_2$]$^+$ cations and uncoordinated ClO$_4^-$ anions and water of crystallization. The geometry around the Cu centers is square-pyramidal; they are linked together by a symmetrical end-to-end-coordinated azido ligand. The spins of the two Cu(II) centers are strongly antiferromagnetically coupled (J = −331 (10) cm^{-1}). **2** crystallizes in the monoclinic system, space group $P2_1/n$, with a = 7.972 (2) Å, b = 11.663 (5) Å, c = 12.053 (4) Å, β = 91.96 (3)°, and Z = 4. The structure was refined to a final R value of 0.036 for 2857 unique reflections. The structure consists of monomeric LCu(N$_3$)$_2$ molecules, which are packed in pairs in the solid state. The geometry around the Cu center is square-pyramidal. No magnetic exchange interactions between the Cu centers have been observed at temperatures between 100 and 300 K. **3** crystallizes in the monoclinic system, space group $C2/c$, with a = 23.63 (1) Å, b = 7.852 (3) Å, c = 16.384 (5) Å, β = 93.68 (3)°, and Z = 4. The structure was refined to a final R value of 0.061 for 1724 reflections. The structure consists of binuclear [L$_2$Cu$_2$(μ-N$_3$)$_2$(ClO$_4$)$_2$] where the two Cu centers are connected via two symmetrical end-to-end-coordinated azido bridges. One perchlorate anion is weakly bonded to each copper ion via one oxygen atom. The geometry around the Cu centers is tetragonally elongated octahedral. **3** is strongly antiferromagnetically coupled ($J < -400$ cm^{-1}). **4** crystallizes in the monoclinic system, space group $P2_1/n$, with a = 13.626 (3) Å, b = 7.875 (2) Å, c = 14.415 (5) Å, β = 113.11 (2)°, and Z = 4. The structure was refined to a final R value of 0.056 for 2447 unique reflections. The structure consists of neutral molecules L′Cu(N$_3$)$_2$, which are packed in pairs in the crystal. The geometry around the Cu center is square-pyramidal. No magnetic exchange interaction between 100 and 300 K has been detected.

Introduction

In the elucidation of the structures of binuclear copper active sites (type III) in hemocyanins, the azide metabolized forms of the oxidized metalloproteins play an important role.[2–6] The electronic spectra, ESR spectra, resonance Raman spectra, and, most importantly, the magnetic spin exchange interactions of these metazido forms differ in many instances significantly from the respective properties of the oxidized copper-containing protein. Thus, useful information concerning the structure of the active sites may be deduced. A necessary prerequisite of such studies is the detailed knowledge and understanding on a molecular basis of magnetic and spectroscopic properties of well-characterized (X-ray structure) low-molecular-weight binuclear and mononuclear azide-containing copper(II) model compounds. In recent years a large number of azide-bridged copper(II) complexes have been prepared and their magnetic properties have been discussed on various levels of sophistication.[7–16] It is the enormous variation of magnetic exchange interactions leading to diamagnetic, antiferromagnetic (weakly and very strongly coupled), and ferromagnetic azide-bridged copper(II) dimers that lends these materials as ideal probes for the elucidation of magneto–structural correlations in these exchange-coupled systems.[17]

Here we report the syntheses, crystal structures, and magnetic properties of four closely related copper(II) azide complexes. The geometry around the Cu(II) centers is in all four complexes slightly distorted square-based pyramidal; the complexes contain the

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(1) (a) Ruhr-Universität Bochum. (b) Universität Heidelberg.

(2) Solomon, E. I. *Met. Ions Biol.* **1981**, *3*, 41–108.

(3) Free, J. A. *Struct. Bonding* (*Berlin*) **1975**, *23*, 1.

(4) Malkin, R.; Malmström, B. G. *Adv. Enzymol. Relat. Areas Mol. Biol.* **1970**, *33*, 177.

(5) Williams, R. J. P. In *Structure and Function of Hemocyanin*; Bannister, J. V., Ed.; Springer Verlag: West Berlin, Heidelberg, 1977.

(6) *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine: New York, 1983.

(7) Felthouse, T. R.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 444–456.

(8) Drew, M. G. B.; McCann, M.; Nelson, S. M. *J. Chem. Soc., Chem. Commun.* **1979**, 481–482.

(9) Agnus, Y.; Louis, R.; Weiss, R. *J. Am. Chem. Soc.* **1979**, *101*, 3381–3384.

(10) Comarmond, J.; Plumere, P.; Lehn, J. M.; Agnus, Y.; Louis, R.; Weiss, R.; Kahn, O.; Morgenstern-Badarau, I. *J. Am. Chem. Soc.* **1982**, *104*, 6330–6340.

(11) Kahn, O.; Sikorav, S.; Gouteron, J.; Jeannin, S.; Jeannin, Y. *Inorg. Chem.* **1983**, *22*, 2877–2883.

(12) Sikorav, S.; Bkouche-Waksman, I.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 490–495.

(13) Bkouche-Waksman, I.; Boillot, M. K.; Kahn, O.; Sikorav, S. *Inorg. Chem.* **1984**, *23*, 4454–4459.

(14) Angus, Y.; Louis, R.; Gisselbrecht, J. P.; Weiss, R. *J. Am. Chem. Soc.* **1984**, *106*, 93–102.

(15) Matsumoto, K.; Ooi, S.; Nakatsuka, K.; Mori, W.; Suzuki, S.; Nakahara, A.; Nakao, Y. *J. Chem. Soc., Dalton Trans.* **1985**, 2095–2100.

(16) Bkouche-Waksman, I.; Sikorav, S.; Kahn, O. *J. Crystallogr. Spectrosc. Res.* **1983**, *13*, 303–310.

(17) *NATO ASI Ser., Ser. C* **1983**, *No. 140*.

0020-1669/86/1325-2818$01.50/0