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Copper(II) and Nickel(II) Complexes of the Tetra-N-methylated Macrocycle Dibenzocyclam: Synthesis, Crystal Structure, and Kinetics of Formation and Substitution

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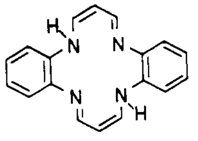
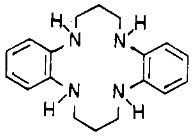
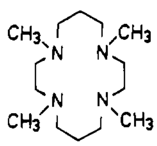
The synthesis of the N_4 macrocyclic ligand 1,4,8,11-tetramethyl-1,4,8,11-tetraazadibenzo[*b,i*]cyclotetradecane (TMBC) and the preparation of the complexes Cu(TMBC)XY (XY = $(ClO_4)_2$, $I(ClO_4)$, $(N_3)(ClO_4)$, $Br(ClO_4)$, $(NO_3)_2$) and $Ni(TMBC)X_2$ (X = ClO_4, Br, NO_3) are reported. It follows from the UV/vis absorption data and the molar conductances of the complexes that in organic solvents except for X = ClO_4 the five-coordinate species $Cu(TMBC)X^+$ is formed. The ligand TMBC and the complexes $Cu(TMBC)(N_3)(ClO_4)$ and $Cu(TMBC)(ClO_4)_2$ have been characterized by a three-dimensional X-ray diffraction study. The ligand TMBC and the complex $Cu(TMBC)(ClO_4)_2$ crystallize in the monoclinic space group $P2_1/c$ with $a = 1198.8$ (5) pm, $b = 812.2$ (3) pm, $c = 2273.8$ (7) pm, $\beta = 115.55$ (1)°, and $Z = 4$ for TMBC and with $a = 1518.7$ (4) pm, $b = 1048.7$ (3) pm, $c = 1668.8$ (4) pm, $\beta = 100.77$ (1)°, and $Z = 4$ for $Cu(TMBC)(ClO_4)_2$. The complex $Cu(TMBC)(N_3)(ClO_4)$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 1564.9$ (3) pm, $b = 1046.3$ (3) pm, $c = 753.1$ (2) pm, $\alpha = 88.71$ (1)°, $\beta = 100.37$ (1)°, $\gamma = 91.53$ (1)°, and $Z = 2$. The copper is five-coordinate in both complexes, with a square-pyramidal arrangement of the donor atoms. The copper lies slightly above the N_4 coordination plane formed by the macrocyclic ligand, the anion azide and perchlorate being coordinated in the top position. All four *N*-methyl groups are located on one side of the N_4 coordination plane, namely the side opposite to where the anion is coordinated. The complex $Ni(TMBC)(NO_3)_2$ is paramagnetic with $\mu_{eff} = 3.18\ \mu_B$. In aqueous solution the various complexes dissociate to form the hydrated species $Cu(TMBC)^{2+}$ and $Ni(TMBC)^{2+}$, respectively. The equilibrium constant K_{an} for the anation reaction $Cu(TMBC)^{2+} + N_3^- \rightleftharpoons Cu(TMBC)(N_3)^+$ is found to be $K_{an} = 30.9 \pm 1.4\ M^{-1}$ at 25 °C and increases with temperature. Through temperature-jump experiments the rate constant k_a for the anation of the cation $Cu(TMBC)^{2+}$ with azide ions to form $Cu(TMBC)(N_3)^+$ is estimated to be $\geq 1 \times 10^6\ M^{-1}\ s^{-1}$ at 20 °C. It is shown by stopped-flow spectrophotometry that formation of the complex $Cu(TMBC)^{2+}$(solv) in DMF from solvated copper(II) ions and TMBC is a two-step process. The first step is first order in both ligand and copper ions with $k_1 = 39.4 \pm 1.2\ M^{-1}\ s^{-1}$ at 25 °C. The slow second step is copper independent with $k_2 = 0.071 \pm 0.004\ s^{-1}$. A mechanism is suggested that ascribes the slowness of the complex formation process to the very limited conformational flexibility of the ligand TMBC.

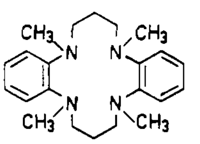
Introduction

Within the large group of tetradentate N_4 macrocycles, the ligand cyclam (1,4,8,11-tetraazacyclotetradecane) can be looked at as a parent compound for many derivatives.[2] As an example, ligand II (often called dibenzocyclam) as obtained through hydrogenation[3] of I is derived from cyclam as well as the tetra-N-methylated ligand III (TMC). As compared to the unsubstituted macrocycle cyclam the introduction of benzo groups or *N*-alkyl groups such as in II and III reduces the flexibility of the 14-membered ring system considerably. As a consequence, complex formation in the system Ni^{2+}/cyclam/Me_2SO is 300-fold faster than in the system Ni^{2+}/III/Me_2SO.[4]


I


II


III (TMC)


IV (TMBC)

This work was undertaken to study the effect of ligand rigidity and steric crowding on the complexation properties of the cyclam type macrocyclic ligand IV, abbreviated as TMBC (*t*etra*m*ethyldi*b*enzo*c*yclam). The new ligand TMBC (1,4,8,11-tetramethyl-1,4,8,11-tetraazadibenzo[*b,i*]cyclotetradecane) was prepared by methylation of II and characterized by a crystal structure determination. TMBC reacts with copper(II) and nickel(II) to form complexes Cu(TMBC)XY and Ni(TBMC)XY (X, Y = monodentate anions). X-ray structures of $Cu(TMBC)(N_3)(ClO_4)$ and $Cu(TMBC)(ClO_4)_2$ are presented as well as kinetic data for the formation of the species $Cu(TMBC)^{2+}$ in DMF and for the substitution of water in the species $Cu(TMBC)(H_2O)^{2+}$ by the azide ion.

Experimental Section

Preparation of TMBC. Macrocycle I (obtained by reaction of 1,2-diaminobenzene with propargylaldehyde) and macrocycle II (obtained by hydrogenation of I) were prepared according to published procedures.[3] N-Methylation of II by standard procedures failed to be successful. TMBC was finally obtained by reductive methylation of II according to Borch and Hassid.[5]

A 15-mL portion of an aqueous solution of formaldehyde (37%), corresponding to 200 mmol of formaldehyde, is added to a solution of 1.46 g of macrocycle II (5 mmol) in 60 mL of MeCN in a three-necked reaction vessel equipped with a reflux condenser. After that, 3 g of $Na[BH_3CN]$ (48 mmol) is added to the stirred solution in 0.5-g portions. The exothermic reaction is initiated by dropwise addition of glacial acetic acid until pH ≈6 (the pH of the aqueous MeCN solution was monitored with wet indicator paper). The reaction mixture is stirred for 1 h at pH ≈6 (if necessary, more glacial acetic

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Table I. Results of Elemental Analysis

		% calcd				% found			
compd	color	C	H	N	M	C	H	N	M
TMBC		74.96	9.15	15.89		75.03	9.14	15.95	
$Cu(TMBC)(ClO_4)_2$	blue	42.97	5.24	9.11	10.33	42.80	5.29	9.50	10.32
$Cu(TMBC)I(ClO_4)$	dark green	41.13	5.02	8.73	9.89	41.11	4.98	8.77	9.65
$Cu(TMBC)(N_3)(ClO_4)$	green	47.20	5.79	17.59	11.40	47.15	5.60	17.84	11.22
$Cu(TMBC)Br(ClO_4)$	turquoise green	44.38	5.42	9.42	10.67	44.14	5.37	9.48	10.28
$Cu(TMBC)(NO_3)_2$[a]	blue	49.93	5.97	15.57	11.76	48.64	5.96	15.48	11.60
$Ni(TMBC)(ClO_4)_2$	dark brown	43.31	5.28	9.18	9.62	43.07	5.28	9.05	9.60
$Ni(TMBC)Br_2$	dark green	46.27	5.65	9.82	10.28	46.07	5.83	9.51	10.30
$Ni(TMBC)(NO_3)_2$	blue	49.37	5.98	15.69	10.97	49.02	6.15	15.58	11.30

[a] An oxygen determination gave 17.8% of O (17.76% calcd).

acid is added). After that, another 1.4 g of $Na[BH_3CN]$ (23 mmol) is added in small portions, the pH is again adjusted to 6 by addition of glacial acetic acid, and the solution is stirred for 2 h at pH ≈6. Finally, the solution is cooled and evaporated to dryness. The solid residue is suspended in 50 mL of 2 M KOH and extracted three times with 50 mL of ether. The ether phase is extracted three times with 50 mL of 2 M HCl. The aqueous phase is cooled with ice, then neutralized by addition of solid KOH, and again extracted three times with 50 mL of ether. If the ether phase is still yellow, it is shaken with charcoal, filtered, dried with K_2CO_3, and evaporated to dryness. A viscous, slightly yellow residue is obtained, which is dissolved in dry ether. After addition of a limited volume of MeOH (limitation: the solution should not become cloudy), the solution is kept in the refrigerator for 4 days, whereupon 1.03 g of colorless crystals are formed: mp 70 °C; yield 58%.

$Cu(TMBC)(ClO_4)_2$. A solution of 2.22 g of $Cu(ClO_4)_2 \cdot 6H_2O$ (6 mmol) in 50 mL of EtOH is slowly added to a refluxing solution of 1.41 g of TMBC (4 mmol) in 75 mL of EtOH, whereupon the color changes to blue-violet and a blue precipitate is formed. After 0.5 h of further refluxing, the reaction mixture is cooled and filtered: yield (after drying over P_2O_5) 2.31 g of $Cu(TMBC)(ClO_4)_2$ (3.76 mmol, 94%); dec pt >300 °C.

$Cu(TMBC)I(ClO_4)$. A solution of 0.38 g of NaI (2.5 mmol) in 20 mL of water is slowly added to a hot solution of 0.62 g of $Cu(TMBC)(ClO_4)_2$ (1 mmol) in 100 mL of water. Upon addition, the color changes from blue to green and a dark green precipitate is formed. After 0.5 h of further heating and stirring, the solution is cooled. Filtration and drying over P_2O_5 give 0.6 g of crystalline $Cu(TMBC)I(ClO_4)$ (93%), mp >300 °C.

$Cu(TMBC)(N_3)(ClO_4)$. This green complex was prepared as described for $Cu(TMBC)I(ClO_4)$, with 2.5 mmol of NaN_3 instead of NaI: yield 95%; mp >300 °C.

$Cu(TMBC)Br(ClO_4)$. This turquoise green complex was prepared as described for $Cu(TMBC)I(ClO_4)$, with 4 mmol of NaBr instead of 2.5 mmol of NaI: yield 95%; mp >300 °C.

$Cu(TMBC)(NO_3)_2$. A solution of 0.97 g of $Cu(NO_3)_2 \cdot 3H_2O$ (4 mmol) in 80 mL of EtOH is slowly added to a hot solution of 1.06 g of TMBC (3 mmol) in 75 mL of EtOH, whereupon the color changes from turquoise green to blue and a blue precipitate is formed. Further refluxing for 0.5 h, cooling, filtration, and drying give 1.55 g of light blue, microcrystalline $Cu(TMBC)(NO_3)_2$: 2.9 mmol (95%); mp >300 °C.

$Ni(TMBC)(ClO_4)_2$. A solution of 0.77 g of $Ni(ClO_4)_2 \cdot 6H_2O$ (2.1 mmol) in 35 mL of EtOH is dropwise added to a refluxing solution of 0.71 g of TMBC (2 mmol) in 50 mL of EtOH. Upon addition, the color changes to dark brown. After further refluxing for 4 h, the solution is concentrated to half of its initial volume. The dark brown, microcrystalline precipitate formed after 1 day of standing is filtered and recrystallized from plenty of hot water: yield (after drying over P_2O_5) 0.67 g of $Ni(TMBC)(ClO_4)_2$ (1.1 mmol, 55%); mp >300 °C.

$Ni(TMBC)Br_2$. A solution of 0.57 g of $NiBr_2 \cdot 3H_2O$ (2.1 mmol) in 200 mL of EtOH is dropwise added to a refluxing solution of 0.71 g of TMBC (2 mmol) in 40 mL of EtOH. The color changes to green without formation of a precipitate. After further refluxing for 4 h, the slightly cloudy solution is concentrated to approximately 10 mL in a rotary evaporator at slightly elevated temperature. Upon cooling, 0.9 g of dark green, microcrystalline $Ni(TMBC)Br_2$ is slowly formed: 1.6 mmol (80%); mp >300 °C.

$Ni(TMBC)(NO_3)_2$. A solution of 0.16 g of $Ni(NO_3)_2 \cdot 6H_2O$ (0.53 mmol) in 25 mL of ethylene glycol dimethyl ether (EGDM) is slowly (within 1 h) added to a solution of 0.17 g of TMBC (0.49 mmol) in 20 mL of EGDM kept at 50 °C. After addition of the first drops, a light blue precipitate is formed. The precipitate is filtered after 15 min of further stirring at 50 °C and recrystallized from EtOH/*n*-heptane (1:1): yield 0.17 g of crystalline $Ni(TMBC)(NO_3)_2$ (66%); dec pt >280 °C.

If the preparation of $Ni(TMBC)(NO_3)_2$ is carried out at a temperature considerably higher than 50 °C, part of the light blue precipitate changes to a brown powder that could not be characterized satisfactorily.

Elemental Analysis. The analytical data obtained for the ligand and for the complexes are summarized in Table I.

Measurement of Conductance. The data were obtained at 25 °C with an instrument produced by Wissenschaftlich Technische Werkstätten/Weilheim (Model LF 530).

Measurement of Magnetic Susceptibility. The susceptibility of the complex $Ni(TMBC)(NO_3)_2$ in the temperature range 2.6–181.2 K was determined with a vibration magnetometer (Institut für Festkörperphysik, Technische Hochschule Darmstadt) described elsewhere[6] at a field strength of 10 kG.

UV/Vis Absorption Spectra. The spectra were recorded with a Zeiss DMR 22 spectrometer at concentrations from 10^{-2} to 5×10^{-5} M in quartz cells with a path length of 0.2–4 cm.

Determination of the Equilibrium Constant K_{an}. The equilibrium constant K_{an} for the anation reaction (1) was determined spectrophotometrically at 25.0, 46.6, and 79.5 °C by recording the absorbance A at $\lambda = 440$ nm at different concentrations of azide ion and fitting to eq 2[7] (A_0 and A_∞ correspond to the absorbance of pure $Cu(TMBC)H_2O^{2+}$ and pure $Cu(TMBC)N_3^+$, respectively).

$$Cu(TMBC)(H_2O)^{2+} + N_3^- \underset{k_d}{\overset{k_a}{\rightleftharpoons}} Cu(TMBC)N_3^+ + H_2O \quad K_{an} = k_a/k_d \tag{1}$$

$$K_{an} = \frac{A - A_0}{A_\infty - A}[N_3^-]^{-1} \tag{2}$$

The spectra were taken at constant pH (≈4.6) by adding HNO_3 and thus producing the buffer system HN_3/N_3^-. The ionic strength was kept at $I = 0.1$ M (KNO_3). The data obtained are as follows: $K_{an} = 30.9 \pm 1.4$ M^{-1} (25 °C); $K_{an} = 31.9 \pm 2.2$ M^{-1} (46.6 °C); $K_{an} = 35.6 \pm 1.8$ M^{-1} (79.5 °C). From these numbers, the enthalpy of formation of the species $Cu(TMBC)N_3^+$ from the species $Cu(TMBC)(H_2O)^{2+}$ is $\Delta H_f = 2.3 \pm 0.6$ kJ mol^{-1}.

X-ray Structure Determinations. The crystal of TMBC selected for the structural analysis was one obtained by recrystallization from ether/MeOH, whereas the crystals of $Cu(TMBC)(N_3)(ClO_4)$ and $Cu(TMBC)(ClO_4)_2$ were grown from aqueous solution. The approximate dimensions of the crystals were 0.25 × 0.25 × 0.5 mm (TMBC), 0.1 × 0.15 × 0.3 mm ($Cu(TMBC)(ClO_4)_2$), and 0.1 × 0.3 × 0.25 mm ($Cu(TMBC)(N_3)(ClO_4)$).

Intensities were measured with a four-circle diffractometer (Siemens-Stoe) using graphite-monochromated Mo Kα radiation ($\lambda = 71.069$ pm). Cell constants were determined by least squares from the 2θ angles of about 50 reflections ($T = 24$ °C), measured on the same instrument.

The measured intensities were corrected for background and *Lp* effects; a numerical absorption correction was applied in the case of

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Table II. Summary of Crystal Data and Intensity Collection for TMBC, Cu(TMBC)$(ClO_4)_2$, and Cu(TMBC)$(N_3)(ClO_4)$

symbol	TMBC	Cu(TMBC)$(ClO_4)_2$	Cu(TMBC)$(N_3)(ClO_4)$
formula	$C_{22}H_{32}N_4$	$C_{22}H_{32}Cl_2CuN_4O_8$	$C_{22}H_{32}ClCuN_7O_4$
mol wt	352.50	614.97	557.54
a, pm	1198.8 (5)	1518.7 (4)	1564.9 (3)
b, pm	812.2 (3)	1048.7 (3)	1046.3 (3)
c, pm	2273.8 (7)	1668.8 (4)	753.1 (2)
β, deg	115.55 (1)	100.77 (1)	100.37 (1); $\alpha = 88.71$ (1)°, $\gamma = 91.53$ (1)°
space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$
Z	4	4	2
d_{calcd}, g cm^{-3}	1.17	1.56	1.53
reflcns collcd (2θ range up to 50)	4027	9253	4624
sym-indep reflcns	3516	4595	4265
reflcns with $F > 2\sigma(F)$	2336	3225	3440
$R_1 = \Sigma\lvert F_o - F_c\rvert/\Sigma\lvert F_o\rvert$	0.077	0.082	0.056
$R_2 = \Sigma w^{1/2}\lvert F_o - F_c\rvert/\Sigma w^{1/2}\lvert F_o\rvert$	0.053	0.049	0.040
abs coeff, cm^{-1}	0.38	10.29	9.94

Table III. UV/Vis Absorption Data for the Complexes M(TMBC)XY (M = Cu(II), Ni(II); X, Y = Monodentate Anions) and for the Ligand TMBC

complex	solvent	λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1})
Cu(TMBC)$(ClO_4)_2$	H_2O	580 (200), 332 sh (1730), 282 (8650), 245 sh (3600)
	CH_3NO_2	555 (160)
	CH_3CN	561 (215)
	DMF	586 (123)
	Me_2SO	583 (136)
Cu(TMBC)$(N_3)(ClO_4)$	H_2O	578 (201), 333 sh (1770), 280 (6900), 240 sh (2600)
	CH_3NO_2	751 (215), 423 (1590)
Cu(TMBC)Br(ClO_4)	H_2O	576 (185), 331 sh (1725), 280 (8110), 240 sh (3180)
	CH_3NO_2	640 (256)
Cu(TMBC)I(ClO_4)	H_2O	578 (191), 328 sh (1700)
	CH_3NO_2	624 (202), 540 sh (120), 460 sh (164)
Cu(TMBC)$(NO_3)_2$	H_2O	580 (200), 330 sh (4000), 282 (8300), 245 sh (3450)
	CH_3NO_2	590 (125)
	C_2H_5OH	670 sh (111), 590 (129), 289 (6500), 243 sh (3400)
Ni(TMBC)$(ClO_4)_2$	H_2O	980 (13), 483 (251), 456 sh (205), 340 sh (165)
	CH_3NO_2	492 (229), 464 (204)
Ni(TMBC)Br_2	CH_3NO_2	665 (55.5), 474 sh (24), 407 (141)
Ni(TMBC)$(NO_3)_2$	H_2O	622 (14), 382 (35)
	CH_3NO_2	985 (14), 610 (29), 380 (54)
	CH_3OH	1000 (13), 615 (24), 385 (43)
TMBC	C_2H_5OH	340 (2600), 299 (6200), 267 (14 700), 241 (27 600)

the azide complex Cu(TMBC)$(N_3)(ClO_4)$.

The structures were solved by direct methods and atomic positions and anisotropic temperature factors refined by least squares to the *R* values given in Table II. Final parameter shifts were less than 0.1 standard deviation. Hydrogen atoms were positioned geometrically (C–H distance 96 pm) and not refined. The crystallographic calculations were performed with the program SHELX 76 modified for use at a small computer (Data General NOVA 3). The final refinement was performed with a program system developed by H. Langhof at Stoe + Cie. (Darmstadt). Table II summarizes relevant crystallographic data and information on data processing. The final positional parameters are given in Table V and bond distances and bond angles in Table VI. Listings of thermal parameters and observed and calculated structure factors are available as supplementary material.

Kinetics of Complex Formation. The formation of the species Cu(TMBC)$^{2+}$ from TMBC and $Cu(ClO_4)_2 \cdot 6DMF$[8] was studied in DMF at 25 °C with a modified[9] DURRUM D110 stopped-flow spectrophotometer in combination with a transient recorder and desk computer. The solvent DMF was distilled under nitrogen at reduced pressure before use. The kinetic runs were done under pseudo-first-order conditions ($[Cu^{2+}] \geq 50[TMBC]$) at $[H_2O] \leq 5 \times 10^{-3}$ M (Karl Fischer titration), and the reaction was monitored at 582 nm. Reproducible runs were evaluated by fitting a total of 100 data points to the sum of two exponential functions with a computer program based on the least-squares method.

Table IV. Molar Conductances of the Complexes at 20 °C

complex	solvent	[complex], 10^{-4} M	Λ, Ω^{-1} cm^2 mol^{-1}	type of electrolyte[a]
Cu(TMBC)$(ClO_4)_2$	H_2O	10	208	1:2
	CH_3NO_2	10	150	1:2
		1	174	
Cu(TMBC)$(N_3)(ClO_4)$	CH_3NO_2	5	83	1:1
			94	
Cu(TMBC)Br(ClO_4)	CH_3NO_2	5	82	1:1
		1	92	
Cu(TMBC)I(ClO_4)	CH_3NO_2	5	93	1:1
		1	109	
Cu(TMBC)$(NO_3)_2$	H_2O	10	210	1:2
		1	225	
	CH_3NO_2	10	85	1:1
		1	94	
	C_2H_5OH	10	36	1:1
Ni(TMBC)$(ClO_4)_2$	H_2O	10	205	1:2
Ni(TMBC)Br_2	H_2O[b]	10	185	1:1 to 1:2
	C_2H_5OH[b]	10	40	1:1
Ni(TMBC)$(NO_3)_2$	H_2O	10	174	1:1 to 1:2
		1	194	
	CH_3NO_2	7	72	1:1
		0.7	67	
	CH_3OH	8	98	1:1 to 1:2
		1.5	121	

[a] Assignment of the type of electrolyte present in solution was made on the basis of the conductance data compiled by: Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81. [b] Data refer to fresh solutions; complex decomposes upon standing of solutions.

Kinetics of Anation. The anation of the species Cu(TMBC)$(H_2O)^{2+}$ with azide ions was studied by the temperature-jump technique with a setup (Max-Planck-Institut für Biophysikalische Chemie, Frankfurt) described elsewhere.[10] The measurements were carried out at constant ionic strength (I = 0.1 M (KNO_3)) and with an excess of NaN_3 ($[NaN_3]$ = 0.04 M; [Cu(TMBC)$(NO_3)_2$] = 1.8 × 10^{-3} M). In agreement with the equilibrium studies described above, a *T*-jump of 5 °C (20–25 °C) produced a change in absorbance of $\Delta A \approx 0.003$ unit.

Results and Discussion

Preparation and Properties of the Complexes. The preparation of the complexes M(TMBC)X_2 with M = Cu(II) and

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Table V. Final Positional Parameters ×10^4 (Excluding Hydrogens)

	$Cu(TMBC)(N_3)(ClO_4)$			$Cu(TMBC)(ClO_4)_2$			TMBC		
atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
N1	6672 (2)	8880 (3)	2661 (5)	3129 (3)	1162 (4)	2779 (3)	3240 (2)	10105 (4)	1254 (1)
C1	7112 (3)	9200 (4)	4528 (6)	3880 (4)	670 (7)	3423 (4)	2488 (3)	10740 (5)	1567 (2)
C2	6567 (3)	10070 (4)	1511 (6)	2547 (4)	73 (6)	2427 (4)	3657 (3)	11432 (4)	952 (2)
C3	7409 (3)	10669 (4)	1140 (7)	2017 (4)	−546 (5)	3001 (4)	4386 (3)	12804 (4)	1422 (2)
C4	7883 (3)	9912 (4)	−60 (7)	1285 (4)	254 (5)	3250 (4)	5586 (3)	12304 (5)	1990 (2)
N2	8252 (2)	8690 (3)	776 (4)	1612 (3)	1406 (4)	3755 (3)	6563 (2)	11866 (3)	1790 (1)
C5	8974 (3)	8978 (4)	2322 (6)	2092 (4)	969 (6)	4590 (4)	6995 (3)	13277 (4)	1546 (2)
C6	8529 (2)	6671 (4)	−563 (5)	827 (4)	2167 (6)	3868 (3)	7558 (3)	10898 (4)	2241 (2)
C7	8912 (3)	5970 (4)	−1730 (6)	49 (5)	1611 (7)	4008 (4)	7797 (3)	10799 (5)	2899 (2)
C8	9389 (3)	6581 (5)	−2884 (6)	−656 (5)	2335 (9)	4116 (4)	8766 (4)	9878 (5)	3337 (2)
C9	9487 (3)	7887 (5)	−2874 (6)	−604 (5)	3635 (8)	4087 (4)	9514 (4)	9044 (5)	3131 (2)
C10	9109 (3)	8600 (4)	−1709 (6)	166 (5)	4198 (7)	3952 (4)	9305 (3)	9101 (5)	2487 (2)
C11	8629 (2)	7982 (4)	−548 (5)	888 (4)	3469 (6)	3828 (4)	8334 (3)	10006 (5)	2022 (2)
N3	8064 (2)	6048 (3)	759 (4)	1739 (3)	4038 (4)	3717 (3)	8138 (2)	10091 (4)	1364 (1)
C12	8727 (3)	5545 (4)	2265 (6)	2243 (4)	4444 (6)	4541 (4)	9145 (3)	9534 (5)	1211 (2)
C13	7504 (3)	4965 (4)	−97 (6)	1551 (4)	5188 (6)	3175 (4)	6930 (3)	9550 (4)	878 (2)
C14	6944 (3)	4324 (4)	1122 (6)	2386 (5)	5784 (6)	2945 (4)	6734 (3)	7682 (5)	847 (2)
C15	6210 (3)	5104 (4)	1545 (6)	2836 (4)	4993 (6)	2387 (4)	5376 (3)	7183 (5)	566 (2)
N4	6493 (2)	6243 (3)	2707 (5)	3273 (3)	3801 (4)	2757 (3)	4733 (2)	7925 (3)	919 (1)
C16	6881 (3)	5810 (4)	4575 (6)	4071 (4)	4139 (7)	3402 (4)	5307 (3)	7570 (5)	1624 (1)
C17	5817 (3)	8304 (4)	2772 (6)	3606 (5)	3064 (7)	2116 (4)	3424 (3)	7723 (5)	632 (2)
C18	5108 (3)	9063 (5)	2903 (6)	4005 (5)	3659 (7)	1527 (5)	2847 (3)	6471 (5)	180 (2)
C19	4329 (3)	8476 (6)	3081 (7)	4337 (5)	2919 (9)	965 (5)	1581 (4)	6236 (5)	−89 (2)
C20	4242 (3)	7181 (6)	3137 (7)	4264 (5)	1619 (8)	985 (5)	868 (3)	7244 (6)	94 (2)
C21	4936 (3)	6429 (5)	3017 (6)	3858 (5)	1034 (7)	1552 (5)	1408 (3)	8508 (5)	532 (2)
C22	5724 (3)	7004 (4)	2806 (6)	3525 (5)	1758 (7)	2138 (5)	2683 (3)	8791 (5)	805 (2)
Cu	7289 (1)	7478 (1)	1469 (1)	2393 (1)	2605 (1)	3206 (1)			
N5	6515 (2)	7606 (4)	−1208 (5)						
N6	5769 (2)	7552 (3)	−1693 (5)						
N7	5019 (3)	7520 (4)	−2157 (7)						
Cl1				787 (1)	2730 (2)	1318 (1)			
O11				1318 (3)	2655 (5)	2105 (2)			
O12				1082 (3)	1774 (4)	823 (3)			
O13				−106 (3)	2543 (6)	1373 (3)			
O14				897 (4)	3966 (4)	1009 (3)			
Cl2	1375 (1)	7552 (1)	3735 (2)	3617 (1)	7414 (2)	452 (1)			
O21	1121 (2)	8746 (3)	4299 (5)	4064 (4)	8491 (5)	195 (4)			
O22	917 (3)	8554 (3)	4378 (6)	4055 (6)	6306 (6)	344 (6)			
O23	1165 (4)	7492 (4)	1876 (6)	3642 (7)	7536 (9)	1250 (4)			
O24	2219 (3)	7411 (5)	4220 (11)	2776 (4)	7335 (9)	73 (5)			

Table VI. Interatomic Distances[a] (pm) and Bond Angles (deg)

$Cu(TMBC)(N_3)(ClO_4)$		$Cu(TMBC)(ClO_4)_2$	
Cu-N1	208.3 (4)	Cu-N1	208.4 (5)
-N2	207.5 (4)	-N2	205.8 (5)
-N3	208.8 (4)	-N3	207.2 (5)
-N4	209.0 (4)	-N4	207.2 (6)
Cu-N5	216.0 (5)	Cu-O11	221.9 (5)
N5-N6	115.9 (6)	Cl1-O11	140.9 (5)
N6-N7	116.4 (6)	-O12	142.3 (6)
d[b]	21.0 (4)	-O13	139.0 (5)
Cu-Cl	>600	-O14	141.6 (6)
N1-Cu-N2	95.5 (2)	*d*[b]	8.9 (5)
-N3	168.8 (2)	Cu-Cl2	>600
-N4	83.0 (2)	N1-Cu-N2	95.6 (3)
N2-Cu-N3	83.5 (2)	-N3	175.1 (4)
-N4	167.7 (2)	-N4	83.9 (2)
N3-Cu-N4	95.6 (2)	N2-Cu-N3	84.2 (2)
N5-Cu-N1	97.8 (2)	-N4	174.2 (4)
-N2	92.5 (2)	N3-Cu-N4	95.8 (3)
-N3	93.2 (2)	O11-Cu-N1	95.3 (3)
-N4	99.8 (2)	-N2	89.3 (2)
Cu-N5-N6	131.0 (3)	-N3	89.3 (2)
N5-N6-N7	177.5 (6)	-N4	96.4 (3)
		Cu-O11-Cl1	167.8 (5)

[a] The numbering of the atoms follows that shown in Figure 3.
[b] The distance *d* describes the extent to which the copper is located above the plane formed by the nitrogen atoms N1, N2, N3, and N4.

Ni(II) can be carried out by simply refluxing an ethanol solution of the ligand TMBC with a slight excess of the salt MX_2. The general procedure for obtaining the mixed-anion complexes $Cu(TMBC)X(ClO_4)$ consists of treating $Cu(TMBC)(ClO_4)_2$ with an excess of the salts NaX in hot water. In the case of the nickel complex $Ni(TMBC)(NO_3)_2$, mild conditions ($T \leq 50$ °C) and the solvent EGDM instead of ethanol favor the formation of a blue product. At higher temperatures this blue complex is converted to a brown powder, which could not be characterized satisfactorily. The results of elemental analysis as compiled in Table I prove the purity of the ligand and of the complexes within the limits of error.

Aqueous solutions of all the different copper complexes prepared appear to have the same blue color. The absorption data summarized in Table III prove indeed that independent of what type of counterion is present in aqueous solution (perchlorate, azide, bromide, iodide, nitrate) all copper complexes have in common a broad d–d absorption band of very similar intensity (ϵ = 185–201 M^{-1} cm^{-1}) with a maximum at λ = 576–580 nm. Furthermore, in the UV range the absorption pattern is again anion independent, with an intense absorption at 280–282 nm and with shoulders at 328–333 nm and at 240–245 nm. One has to conclude, therefore, that all copper(II) complexes studied dissociate in water more or less completely according to (3). In all cases the absorbing species is obviously the same, namely the hydrated cation $Cu(TMBC)^{2+}$.

$$Cu(TMBC)XY \rightleftharpoons Cu(TMBC)^{2+}(aq) + X^- + Y^- \quad (3)$$

The spectra of the solutions of $Cu(TMBC)(ClO_4)_2$ in DMF and Me_2SO resemble those obtained with water as solvent in the sense that again a broad, although less intense d–d ab-

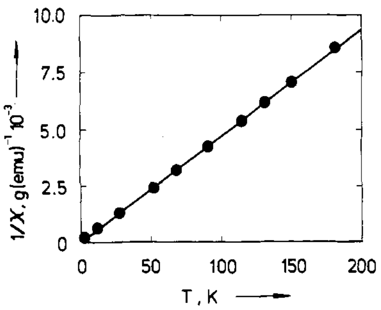

Figure 1. Temperature dependence of the magnetic susceptibility of $Ni(TMBC)(NO_3)_2$ according to the Curie law with a slope yielding $\mu_{eff} = 3.18\ \mu_B$.

sorption is observed, peaking at 586 and 583 nm. In nitromethane and acetonitrile the main absorption band of the perchlorate complex is shifted from 580 to 555 and 561 nm, respectively.

The spectra of the complexes $Cu(TMBC)X(ClO_4)$ with X = N_3, Br, or I and of the complex $Cu(TMBC)(NO_3)_2$ in nitromethane differ considerably from those in water by a strong red-shift of the d–d absorption band observed for water at 580 nm. The red-shift follows the order $N_3^- > Br^- > I^- > NO_3^- > H_2O$ and resembles the shift caused by monodentate axial ligands X and L in the five-coordinate, square-pyramidal complexes[11] Cu(cyclops)X and Cu(cyclops)L$^+$.

The spectral data obtained for aqueous solutions of the two nickel complexes $Ni(TMBC)(ClO_4)_2$ and $Ni(TMBC)(NO_3)_2$ are very different, thus indicating that in contrast to the corresponding copper complexes complete dissociation and formation of the cation $Ni(TMBC)^{2+}(aq)$ is not the common process. The water spectra and also the nitromethane spectra are clearly anion dependent; i.e., the anions are more or less coordinated in solution.

The conductance data compiled in Table IV parallel and support the spectral data. The molar conductances of 208, 210, and 205 $\Omega^{-1}\ cm^2\ mol^{-1}$ obtained for the complexes $Cu(TMBC)(ClO_4)_2$, $Cu(TMBC)(NO_3)_2$, and $Ni(TMBC)(ClO_4)_2$ in aqueous solution are in agreement with a more or less complete dissociation of the complex according to (3) and formation of the complex cations $Cu(TMBC)^{2+}(aq)$ and $Ni(TMBC)^{2+}(aq)$. The dissociation of the complexes $Ni(TMBC)Br_2$ and $Ni(TMBC)(NO_3)_2$ in water, however, appears to be incomplete since the conductances observed lie in between those typically shown by 1:1 and 1:2 electrolytes. When nitromethane and ethanol are applied as solvents, complete dissociation is observed only for the perchlorate complex $Cu(TMBC)(ClO_4)_2$. All the others behave as 1:1 electrolytes, thus indicating the formation of five-coordinate species $Cu(TMBC)X^+$ with X = N_3, Br, I, or NO_3. This behavior is paralleled by the spectroscopic finding that in nitromethane the d–d absorption is strongly red-shifted relative to water as solvent.

It follows from the sum of spectroscopic and conductivity data that all of the copper complexes prepared and also the nickel complex $Ni(TMBC)(ClO_4)_2$ lose both their monodentate anions in water and in very polar solvents such as Me_2SO and DMF, thus forming the species $Cu(TMBC)^{2+}(solv)$ and $Ni(TMBC)^{2+}(aq)$, respectively. In less polar solvents such as nitromethane, except for X = ClO_4 the five-coordinate species of $Cu(TMBC)X^+$ is formed (X = N_3, I, Br, NO_3). This type of behavior is also shown by the complex $Ni(TMBC)(NO_3)_2$ dissolved in nitromethane and resembles very much the behavior of the copper(II) and nickel(II) complexes with the ligand *N*-tetramethylcyclam (III) studied by Barefield et al.[12]

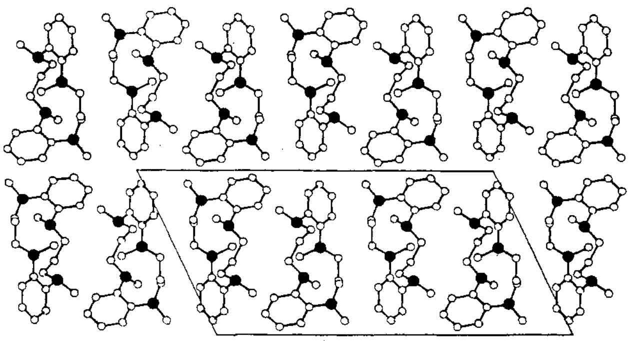

Figure 2. View of the unit cell of the ligand TMBC projected along [010] (the filled circles represent nitrogen atoms).

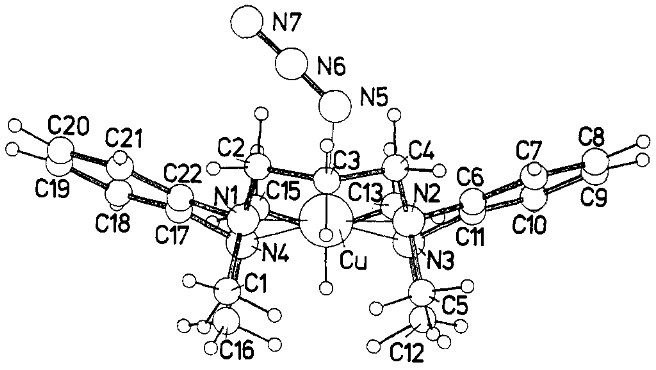

Figure 3. View of the coordination geometry of $Cu(TMBC)(N_3)(ClO_4)$ (atom C14 is hidden behind the copper).

The equilibrium constant K_{an} for anation of the species $Cu(TMBC)(H_2O)^{2+}$ with azide ions according to (1) is in agreement with these findings. With $K_{an} = 30.9\ M^{-1}$ at 25 °C one can calculate that for a 10^{-3} M aqueous solution of the complex $Cu(TMBC)(N_3)(ClO_4)$ the ratio $[Cu(TMBC)(N_3)^+]:[Cu(TMBC)^{2+}(aq)]$ is only 3:97, which means that in water the complex $Cu(TMBC)(N_3)(ClO_4)$ should indeed behave as a 1:2 electrolyte as is observed.

The temperature dependence of the magnetic susceptibility of the nickel complex $Ni(TMBC)(NO_3)_2$ is shown in Figure 1. It follows from the data collected that the complex is high spin in the solid state ($\mu_{eff} = 3.18\ \mu_B$). This result would be in agreement with an octahedral ligand field formed by the N_4 set of donor atoms of the ligand TMBC in a planar arrangement around the nickel and the nitrate anions coordinated in the axial positions. An alternative could be, however, an octahedral ligand field with the ligand TMBC in a somewhat folded form and one nitrate anion occupying two cis positions.

Structural Results. TMBC. Figure 2 (see also Table II) shows a view of the unit cell projected along [010]. This figure clearly shows that the arrangement of the single molecule of TMBC in the crystal lacks any symmetry and regularity. The presence of the two benzo rings and of the four *N*-methyl groups introduces so much steric hindrance that the molecule adopts a very distorted stucture in the solid state and probably also in solution.

$Cu(TMBC)(N_3)(ClO_4)$. The coordination geometry of the complex as shown in Figure 3 is striking in the sense that upon complex formation the symmetry-lacking free ligand is now forced into a highly symmetric arrangement with the four methyl groups bent to one side and the two benzo rings slightly bent to the other side of the N_4 coordination core. The copper is shifted slightly out of the N_4 plane to the side of the benzo rings (d = 21 pm, Table VI), and the azide ion is coordinated on top of the copper with a distance Cu–N5 of 216 pm (see

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(11) Addison, A. W.; Carpenter, M.; Lau, L. K.-M.; Wicholas, M. *Inorg. Chem.* **1978**, *17*, 1545.

(12) Barefield, E. K.; Wagner, F. *Inorg. Chem.* **1973**, *12*, 2435.

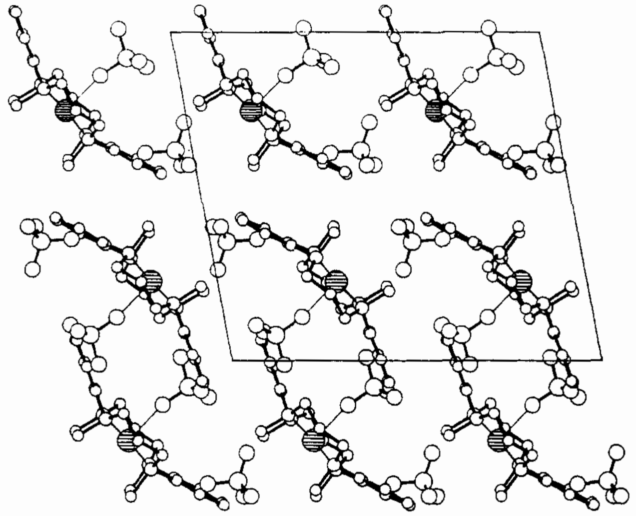

Figure 4. View of the unit cell of $Cu(TMBC)(ClO_4)_2$ projected along [010] (the copper atoms are shaded).

Table VI). The distances between the copper and the four nitrogen atoms of the macrocycle are slightly different with a maximum of 209 pm (Cu–N4) and a minimum of 207.5 pm (Cu–N2). It follows from Figure 3 and from the angles given in Table VI that the coordinated nitrogen atom of the azido ligand is not precisely centered on top of the copper. The copper is clearly five-coordinate with a square-pyramidal arrangement of the nitrogen donor atoms, the second anion perchlorate being noncoordinated (Cu–Cl distance >600 pm).

$Cu(TMBC)(ClO_4)_2$. Figure 4 presents a view of the unit cell projected along [010]. The structural elements found are identical with those obtained for the azido complex $Cu(TMBC)(N_3)(ClO_4)$. One of the two perchlorate anions is coordinated (Cu–O11 distance 222 pm, see Table VI); the second one is not (Cu–Cl2 distance >600 pm). The compound has to be classified as a perchlorato complex, therefore, with a square-pyramidal arrangement of the donor atoms and with a "doming" effect of the perchlorate ion ($d = 9$ pm, see Table VI) less pronounced than that of the azide ion ($d = 21$ pm). The four methyl groups are again found on one side of the N_4 coordination plane, opposite to the coordinated perchlorate ion.

A comparison of these findings with the conductance and spectroscopic data allows a better understanding of what happens in solution. The azide ion in the complex $Cu(TMBC)(N_3)(ClO_4)$ is obviously rather strongly coordinated so that the solvent nitromethane is not able to dissociate it, whereas the solvent water is. The less strongly bound perchlorate ion in $Cu(TMBC)(ClO_4)_2$ however is replaced even in nitromethane solution.

Substantial information on the stereochemical aspects of transition-metal complexes with tetra-N-methylated cyclam III (TMC) as ligand has become available through the work done by Barefield and co-workers. It was concluded from NMR studies that in the species $Zn(TMC)Cl^+$ all four methyl groups are on one side of the coordination plane, the chloride ion being coordinated on the opposite side.[12] The complex prepared by adding hydrated nickel(II) perchlorate to 1 equiv of TMC was shown to have the same stereochemistry with all four methyl groups on one side of the macrocyclic plane.[13] The addition of sodium azide however produces the pentacoordinate species $Ni(TMC)(N_3)^+$ in which the azide ion is coordinated on the same side of the coordination plane, i.e., on the side of the four methyl groups.[13] In contrast to this type of stereochemistry it was found[14] that direct permethylation of the parent complex $Ni(cyclam)^{2+}$ produced the thermodynamically most stable stereochemical isomer in which adjacent pairs of methyl groups are on opposite sides of the N_4 plane.

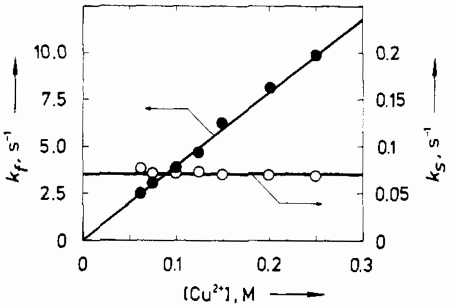

Figure 5. Dependence of rate constants k_f and k_s on copper concentration for reaction 4 studied at 298 K in DMF ($[TMBC] = 10^{-3}$ M) with the slope $k_1 = k_f/[Cu^{2+}] = 39.4 \pm 1.2\ M^{-1}\ s^{-1}$ and an average value of $k_s \equiv k_2 = 0.071 \pm 0.004\ s^{-1}$.

Comparing the stereochemical behavior of the tetra-N-methylated macrocycles TMBC (IV) and TMC (III) on the basis of the complexes $Cu(TMBC)(N_3)(ClO_4)$ and $Ni(TMC)(N_3)(ClO_4)$, one thus finds both similarity and dissimilarity. The kinetically controlled formation of the two complexes from metal salt and TMBC or TMC in solution is similar in the sense that upon coordination the ligands adopt a configuration in which the four methyl groups are all on one side of the N_4 coordination plane. The difference is that for the species $Ni(TMBC)(N_3)^+$ the fifth coordination site is located on the same side, whereas for the species $Cu(TMBC)(N_3)^+$ the azide ion is coordinated on the side opposite to that of the four methyl groups. There is no obvious explanation for this difference. Apart from the fact that the coordination chemistry of Ni(II) and Cu(II) can be quite different one has to be aware of the two benzo rings in TMBC that may significantly alter the properties of the latter ligand as compared to TMC.

Kinetic Studies. The high rate of copper complex formation in solution is in general attributed to the high rate of solvent exchange of solvated copper(II) ions. So, if the rate of formation of a given copper complex is considerably slower than expected on the basis of $k_{ex} \approx 10^9\ s^{-1}$ (k_{ex} = rate constant for water exchange of copper(II) ions), processes other than solvent replacement become rate controlling. These can be deprotonation steps[15] or sterically hindered steps.

The rate of formation of the species $Cu(TMBC)^{2+}(solv)$ from $Cu^{2+}(solv)$ and TMBC lies on the stopped-flow time scale. In solvent mixtures of ethanol and water and with an excess of the ligand ($[Cu^{2+}] \leq 0.01[TMBC]$), the time dependence of the absorbance at 580 nm is composed of an initial fast step and several slower consecutive steps that are probably associated with protonated ligand species. The kinetics of complex formation appear to be simpler in an aprotic polar solvent such as DMF. In this solvent and with an excess of the metal ($[Cu^{2+}] \geq 50[TMBC]$), the increase in absorbance at 582 nm with time is made up of two contributions. The absorbance/time data can be properly fitted to the sum of two exponential functions. The first one, as characterized by rate constant k_f, describes a relatively fast process covering approximately 80% of the total change in absorbance. As shown in Figure 5 rate constant k_f is first order in copper concentration, i.e., $k_f = k_1[Cu^{2+}]$ with $k_1 = 39.4 \pm 1.2\ M^{-1}\ s^{-1}$. The second process, as characterized by rate constant k_s, is considerably slower and contributes only 20% of the total change

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(13) D'Aniello, M. J., Jr.; Mocella, M. T.; Wagner, F.; Barefield, E. K.; Paul, I. C. *J. Am. Chem. Soc.* **1975**, *97*, 192.

(14) Wagner, F.; Mocella, M. T.; D'Aniello, M. J., Jr.; Wang, A. H.-J.; Barefield, E. K. *J. Am. Chem. Soc.* **1974**, *96*, 2625.

(15) Heim, G.; Elias, H. *Z. Phys. Chem. (Wiesbaden)* **1981**, *128*, 197.

in absorbance. Rate constant k_s is independent of the copper concentration, so that $k_s \equiv k_2 = 0.071 \pm 0.004$ s^{-1} (see Figure 5). Since the overall rate of reaction 4 in the aprotic solvent

$$Cu^{2+}(solv) + TMBC \rightarrow Cu(TMBC)^{2+} \qquad (4)$$

DMF is much slower than expected[16] for the solvent exchange in the species $Cu(DMF)_6^{2+}$ on the basis of $k_{ex} \approx 10^{8.5}$ s^{-1} and since the ligand TMBC is rather rigid, one has to introduce steric arguments to explain the slowness of the reaction.

The complex formation presumably starts with the coordination of TMBC as a monodentate, sterically hindered ligand to form a species Cu–(TMBC)$^{2+}$ according to the Eigen–Wilkins mechanism:

$$Cu^{2+}(solv) + TMBC \rightleftharpoons \{Cu,TMBC\}^{2+} \quad K_{os} \qquad (5)$$

$$\{Cu,TMBC\}^{2+} \xrightarrow{k_{ex} \approx 10^{8.5}\ s^{-1}} Cu\text{–}(TMBC)^{2+} \qquad (6)$$

This process is very fast and equilibrium 7 is probably established before the observation on the stopped-flow time scale begins.

$$Cu^{2+}(solv) + TMBC \rightleftharpoons Cu\text{–}(TMBC)^{2+} \quad K_1 \qquad (7)$$

Due to the inflexibility of the ligand TMBC, however, constant K_1 is supposedly much smaller than to be expected for normal tertiary amines.

The formation of further Cu–N bonds can take place only when the singly bonded N_4 macrocycle in the species Cu–(TMBC)$^{2+}$ finds itself in a conformation and spatial arrangement relative to the copper to allow ring closure. It is well conceivable that the partially coordinated macrocycle is subject to a conformational equilibrium (8) preceding the formation of further Cu–N bonds:

$$Cu\text{–}(TMBC)^{2+} \rightleftharpoons Cu\text{–}(TMBC')^{2+} \quad K_{conf} \qquad (8)$$

$$Cu\text{–}(TMBC')^{2+} \xrightarrow{k_{ex}} Cu(TMBC)^{2+}(int) \qquad (9)$$

The species Cu(TMBC)$^{2+}$(int) is an intermediate in the sense that it is still lacking the high degree of symmetry found for the solid state. Its formation represents the first, copper-dependent step of the two steps experimentally observed. If so, the observed rate constant k_1 is related to the sequence (7)–(9) according to $k_1 = K_1 K_{conf} k_{ex}$ and the small size of k_1 relative to k_{ex} is caused by a small value of K_{conf} as well as of K_1 (equilibrium constant for the coordination of TMBC as a monodentate ligand). In agreement with the interpretation found in the literature for similar systems[4,18] it is suggested that the final step (10) is a slow, copper-independent step in

$$Cu(TMBC)^{2+}(int) \xrightarrow{k_2} Cu(TMBC)^{2+} \qquad (10)$$

which the unfavorably coordinated ligand of the intermediate rearranges itself to let the methyl groups and benzo rings have the orientation shown in Figures 3 and 4.

It has been found[17] that in an ethanol/water mixture (10:1) dibenzocyclam (II) reacts with copper(II) approximately 25 times slower than cyclam. The introduction of the benzo rings obviously reduces the flexibility and, hence, the reactivity of the macrocyclic ligand. Comparative studies on the kinetic effect of N-methylation were carried out by Hertli and Kaden[4] in the systems Ni^{2+}/cyclam/DMF and Ni^{2+}/TMC/DMF. It was found that the rate of the reaction of cyclam with nickel(II) in DMF can still be explained on the basis of a dissociative model in which the substitution of a solvent molecule in the $Ni(DMF)_6^{2+}$ ion is rate controlling. It turned out that the tetra-N-methylated ligand TMC (III) is slower in complex formation by a factor of 22.5. Unfortunately, there are no rate data for the systems Cu^{2+}/cyclam/DMF and Cu^{2+}/TMC/DMF that would allow proof that the rate of reaction 4 studied in this work cannot be explained by assuming that the strong retardation observed for the ligand TMBC is simply the addition of the retarding effects of the methyl groups and of the benzo rings. Obviously, the introduction of both methyl groups and benzo rings makes the ligand extremely rigid and unreactive.

The two-step complex formation described above (see eq 7–10) is also found for the reaction of cyclam with nickel(II) in DMF,[4] Me_2SO,[4] and acetonitrile[18] and for the reaction of several N_2O_2 macrocycles with nickel(II) in methanol.[19] In all cases there are a metal-dependent incorporation step and a metal-independent rearrangement step.

In the azido complex Cu(TMBC)(N_3)(ClO_4), the copper is five-coordinate, with the azide ion sitting on top of the copper (see Figure 3). In aqueous solution the azide ion dissociates and at 25 °C equilibrium 1 is characterized by $K_{an} = 30.9$ M^{-1} (see Experimental Section).

An attempt was made to determine the rate of water replacement by a temperature-jump experiment. As a result, the rate of anation was found to be close to the limits of resolution of the apparatus applied. Under the experimental conditions described above a relaxation time of $\tau = 16$ µs was estimated that corresponds to a rate constant $k_a \geq 1 \times 10^6$ M^{-1} s^{-1}. Although the water position is somewhat shielded through the two benzo rings, its rate of replacement is still very high. The number obtained is smaller than that found for the anation of the $Cu(H_2O)_6^{2+}$ ion with ammonia[20] ($k_a = 2 \times 10^8$ M^{-1} s^{-1}) but much greater than that found for the anation of the Cu(Me_6tren)$^{2+}$ cation with azide[21] ($k_a = 840$ M^{-1} s^{-1}). Herron and Moore found[22] on the basis of ^{13}C NMR studies that the rate of acetonitrile exchange in the species Ni(TMC)(CH_3CN)$^{2+}$ (carrying all the methyl groups on one side of the coordination plane) is very high as well. The rate constant for the exchange of a single solvent molecule is $k_{ex} = 5.2 \times 10^6$ s^{-1}.

It should be mentioned finally that the blue nickel complex Ni(TMBC)(NO_3)$_2$ obtained at relatively low temperature reacts with the bidentate ligand "phen" in methanol in a two-step reaction that can be followed by stopped-flow techniques. Although the product of this reaction could not be characterized satisfactorily, it is interesting to note that the species Ni(TMBC)(NO_3)$^+$ or Ni(TMBC)$^{2+}$ obtained upon dissolution of the complex Ni(TMBC)(NO_3)$_2$ in methanol can add a cis-coordinating bidentate ligand. This does point to a nonplanar arrangement of the four nitrogen atoms of the ligand in the complex Ni(TMBC)(NO_3)$_2$.[23]

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(23) After submission of the paper, an X-ray diffraction study on a single crystal of the blue complex Ni(TMBC)(NO_3)$_2$ was carried out (Grewe, R.; Paulus, H.; Klaehn, D.-D.; Elias, H., to be submitted for publication). In agreement with the coordination of the bidentate ligand "phen" observed kinetically, it was found that the nickel is six-coordinate with a N_4O_2 set of donor atoms and that indeed one of the two nitrate ions is coordinated as a bidentate ligand, occupying two cis positions of the distorted octahedron (the distances Ni–O1 and Ni–O2 are 213.6 and 216.3 pm, respectively).

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Registry No. II, 22119-38-6; IV, 88106-41-6; Cu(TMBC)$(ClO_4)_2$, 88106-43-8; Cu(TMBC)I(ClO_4), 88106-45-0; Cu(TMBC)$(N_3)(ClO_4)$, 88106-47-2; Cu(TMBC)Br(ClO_4), 88106-49-4; Cu(TMBC)$(NO_3)_2$, 88106-51-8; Ni(TMBC)$(ClO_4)_2$, 88106-53-0; Ni(TMBC)Br_2, 88106-54-1; Ni(TMBC)$(NO_3)_2$, 88106-56-3; Cu(TMBC)$(H_2O)^{2+}$, 88106-57-4; Cu(TMBC)N_3^+, 88106-46-1; Cu(TMBC)$^{2+}$, 88106-58-5.

Supplementary Material Available: Listings of observed and calculated structure factors and atomic parameters for TMBC, Cu(TMBC)$(N_3)(ClO_4)$, and Cu(TMBC)$(ClO_4)_2$ (105 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Spectrochimie des Eléments de Transition, Université de Paris Sud, 91405 Orsay, France, and Laboratoire de Chimie Structurale des Matériaux, Université Pierre et Marie Curie, 75232 Paris, France

Crystal Structure and Magnetic and EPR Properties of Bis(μ-azido)tetrakis(4-*tert*-butylpyridine)dicopper(II) Perchlorate: A New Copper(II) Dinuclear Complex with a Large Stabilization of the Ground Triplet State

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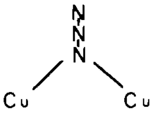
The title compound of formula $[Cu_2(t\text{-Bupy})_4(N_3)_2](ClO_4)_2$, with *t*-Bupy = 4-*tert*-butylpyridine, has been synthesized, and its structure has been solved at room temperature. It crystallizes in the monoclinic system, of space group $P2_1/c$. Its lattice constants are a = 12.819 (3) Å, b = 13.76 (1) Å, c = 13.65 (1) Å, and β = 100.00 (2)° with Z = 2 dimeric units. The structure consists of $[Cu_2(t\text{-Bupy})_4(N_3)_2]^{2+}$ dimeric cations and noncoordinated perchlorate anions. The copper(II) ions are fourfold coordinated with planar surroundings. They are bridged by azido groups in an end-on fashion. The Cu···Cu separation is 3.045 (3) Å, and the Cu–N–Cu bridging angle is 100.5 (6)°. The magnetic properties of the compound have been studied in the 2–300 K temperature range. They revealed that the ground state is the spin-triplet state, with a separation of 105 ± 20 cm^{-1} with regard to the low-lying spin-singlet state. The EPR powder spectrum confirms the nature of the ground state. On the assumption that the **D** and **g** tensor axes were coincident, this spectrum was interpreted with axial and rhombic zero-field splitting parameters, D = 0.42 (5) cm^{-1} and E = 0.02 (5) cm^{-1}. A new investigation of the magnetic properties of the copper azide $Cu(N_3)_2$ is also reported. This compound orders antiferromagnetically at T_N = 124 K. It is pointed out that this result is in no way a counterexample of the specific ability of the end-on azido bridges to stabilize the triplet state in copper(II) dinuclear complexes.

Introduction

Likely the most fascinating aspect of the chemistry of the μ-azido copper(II) dinuclear complexes is the versatility of their magnetic properties. In bibridged complexes with one or two end-on azido bridges like **1**, the interaction between the metal ions is strongly ferromagnetic and the energy gap between ground spin triplet and excited spin singlet may be so large that even at room temperature the S = 0 state is weakly populated.[2,3] In complexes with one or two end-to-end bridges like **2**, the interaction is strongly antiferromagnetic and the singlet state may be so stabilized with regard to the excited triplet state that the compound appears diamagnetic.[4,5] Finally, in complexes with asymmetric end-to-end azido bridges like **3**, with a short Cu–N$_\alpha$ bond and a long Cu–N$_\beta$ bond, the interaction is negligible when the geometry around the copper(II) ion is square pyramidal[2,6] or very weakly antiferromagnetic when this geometry tends to the trigonal bipyramid.[7] To rationalize these behaviors, two explanations have been proposed that correspond to two levels of sophistication of a same conceptual approach. The first theoretical approach only took into account the magnetic orbitals centered on each metal ion and the molecular orbitals constructed from them;[2] the second approach accounted for the role of the low-energy doubly occupied orbitals with a preponderant ligand character.[3] It has been shown that in the case of the azido bridges this could lead to a *spin-polarization effect*, due to the nature of the π_g HOMOs of N_3^-. Each π_g orbital[8] describes two paired electrons localized at the two extremities of N_3^-. At each instant, one of the two electrons has an α spin and the other one a β spin. When N_3^- bridges as in **1**, a π_g electron on the bridging nitrogen atom is partially delocalized toward the two d_{xy} metal orbitals; this favors the situation where the two metallic unpaired electrons are parallel, therefore the ferromagnetic interaction. In contrast, when N_3^- bridges as in **2**, an α-spin electron is partially delocalized toward a metal center and a β-spin electron is partially delocalized toward the other



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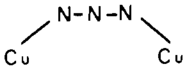

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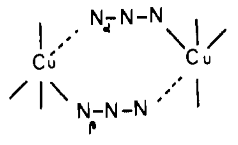

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