Since the hexagonal phase is undistorted, one would not expect the formation of dimers to occur, thus reducing the effect in $Rb_{0.20}CrF_3$ and $Rb_{0.25}CrF_3$. The magnetic properties (except for C_M) may also be altered somewhat by structural defects that are expected to be even more common in Rb_xCrF_3 than in Rb_xVF_3.

Conclusions

The Rb_xCrF_3 system ($x = 0.18$–0.29) forms a Magneli hexagonal bronze-like lattice similar to the Rb_xVF_3 system. Ordering of partially filled Rb^+ sites forms superlattice structures in which sites are $^1/_2$, $^2/_3$, or $^3/_4$ filled. These superstructures are composition dependent and are optimum at compositions where $x = 0.18$, 0.225, and 0.25, respectively. Cooperative Jahn–Teller ordering of the Cr^{2+} ion is also composition dependent as it is associated with the superstructures $\alpha(0.222)$ and $\alpha(0.250)$. This leads to the conclusion that Cr^{2+}–Cr^{3+} electronic ordering exists in these two phases.

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Unusual Redox and Chemical Properties of a Sterically Constrained N_3Cu^{II} Center. Preparation, Structure, and Solution Studies of (Nitrato)(1,4,7-triazacyclododecane)copper(II) Nitrate

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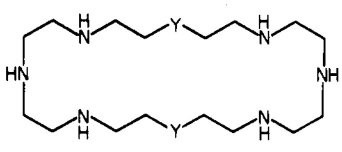
Dark blue crystals of $[Cu(TCD)(NO_3)](NO_3)$, TCD = 1,4,7-triazacyclododecane, form in the reaction of the free ligand with cupric nitrate in methanol. Linking of the terminal nitrogen atoms of the diethylenetriamine fragment of the TCD "minicycle" by a pentamethylene chain provides a steric constraint that substantially affects the properties of the $Cu(TCD)^{2+}$ cation. In particular, $Cu(TCD)^{2+}$ shows a quasi-reversible one-electron oxidation at −185 mV (vs. Fc/Fc^+), as compared with unconstrained $Cu(dien)^{2+}$, dien = 1,4,7-triazaheptane (diethylenetriamine), which exhibits an irreversible wave at an E_p of −450 mV by cyclic voltammetry under identical conditions ($LiClO_4$/acetonitrile solutions). Moreover, optical and electron spin resonance spectroscopic studies suggest that, whereas $Cu(dien)^{2+}$ binds one cyanide ligand strongly in its equatorial plane, $Cu(TCD)^{2+}$ coordinates two such cyanide ligands, with probable decoordination or substantial bond weakening of one of the nitrogen donors of the TCD group. Details of the geometric distortion produced by the TCD ligand were revealed in a single-crystal X-ray diffraction study of $[Cu(TCD)(NO_3)](NO_3)$, which crystallizes in the orthorhombic space group *Pnma*, $a = 14.104$ (2) Å, $b = 8.882$ (3) Å, $c = 12.054$ (1) Å, $V = 1510$ Å^3, and $Z = 4$. The structure is irregular and may be described as trigonal bipyramidal with axial positions occupied by one oxygen atom of a bidentate nitrate ligand and the central nitrogen atom of the TCD group. The major distortion found is the N–Cu–N′ angle of 138.6 (5)°, where N and N′ are related by a crystallographically required mirror plane of symmetry passing through the $[Cu(TCD)(NO_3)]^+$ cation. This angle is too small to span the trans basal positions of the usual tetragonal geometry for Cu(II), the structure adopted by $Cu(dien)^{2+}$ complexes, but not so small as to enforce facial type stereochemistry found with minicycles such as 1,4,7-triazacyclononane. The relevance of these results to copper(II) centers in metalloproteins is discussed.

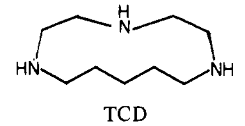
Introduction

Recent efforts in our laboratory have focused on the chemistry of copper(II) in binucleating macrocycles, especially those having hexaaza donor functionalities such as A and A′.[1–3]



A, Y = O
A′, Y = CH_2

The synthetic routes[4] to these macrocycles give as a byproduct the triaza "minicycle" 1,4,7-triazacyclododecane (TCD). We



TCD

were interested to learn how the steric demands of this minicycle, achieved by connecting the terminal nitrogen atoms of the flexible 1,4,7-triazaheptane (diethylenetriamine, dien), would influence the coordination chemistry, spectroscopy, and redox properties of its copper(II) complex. Cupric complexes of cyclic triamines have been investigated by various authors;[5–16] relevant spectroscopic and stability data for these

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Table I. Thermodynamic and Visible Spectroscopic Data for Copper(II) Complexes of Triaza Macrocycles and Diethylenetriamine

ligand	pK_1^H	pK_2^H	pK_3^H	log K_{ML}	λ_{ML}, nm (ϵ_{ML})	pK_{MLOH}	λ_{MLOH}, nm	log K_{ML_2}	λ_{ML_2}, nm (ϵ_{ML_2})	ref
1,4,7-triazaheptane (dien)	10.18	9.41	4.83	16.55	615 (82)	9.49	605 (73)	21, 15	631 (110)	17
1,4,7-triazacyclononane	12.6^a	7.24		17.5	637 (42)	4.51^b	620 (124)	31.5	579 (37)	11
	10.42	6.82		15.5	658	5.25				5, 6
	10.59	6.88		16.2^c						9
					676^d					16
					653 (39)					16
									629^e	12
1,4,7-triazacyclodecane	12.75^a	6.86		16.14	664 (74)	13.48^b	631 (196)	26, 40	632 (44)	10, 11
	12.02	6.59		15.48	662					5, 7
									637^e	12
1,4,7-triazacycloundecane							680^f			12
1,4,7-triazacyclododecane					660 (80)					this work
					725^g		$645,^h$ 709^f			12
1,4,7-triazacyclotridecane					676^g		763^f			12
1,5,9-triazacycloundecane	11.96	7.61		14.44	662, 685				625^i	5, 7
1,5,9-triazacyclododecane	13.15^a	7.97		13.16	689 (138)	14.77^b	649 (285)	20, 84		10
	12.60	7.57	2.41	12.63	694	8.36				5, 7
2,4,4′-trimethyl-1,5,9-triazacyclododecane	12.3	7.34	2.51	11.6	709 (99)	8.5	667 (89)			13
2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene					$699 (162)^j$		$641 (138)^k$			18
1,5,9-triazacyclotridecane							$699,^f$ 633^h			12
1,5,9-triazacyclotetradecane							658^f			12

[a] By NMR. [b] Dimeric species. [c] By polarography. [d] Solid, dibromo. [e] Solid, diperchlorato. [f] Solid, Cl^-/OH^--bridged dimer. [g] Solid, Cl^--bridged dimer. [h] Solid, OH^--bridged dimer. [i] Solid, dinitrato. [j] Dithiocyanato complex in DMF. [k] Hydroxo-bridged dimer in CH_2Cl_2.

and related[17,18] complexes are given in Table I. The effect of ring size on the stability and ligand field absorption spectra of the complexes has been investigated and, from a comparison with open-chain triamines, a facial arrangement of the nitrogen donors leading to a pseudooctahedral copper(II) coordination geometry was suggested.[10,11] X-ray structural information is available for two cupric complexes of 1,4,7-triazacyclononane.[15,16]

In this paper we describe the synthesis, structural characterization, and solution spectroscopic and electrochemical properties of the title compound. Especially interesting are the differences between the redox properties and reactivity with cyanide ion of this compound compared with those of the related, unconstrained $[Cu(dien)]^{2+}$ complex. Information of this kind is valuable for interpreting data on copper centers in protein active sites such as met apo hemocyanin.[19]

Experimental Section

Materials. Solvents used were of spectrograde quality. The copper salt $Cu(NO_3)_2{\cdot}2.5H_2O$ was analytical grade, and all other chemicals were of the highest purity available. 1,4,7-Triazacyclododecane (TCD) was obtained as a byproduct of the synthesis of 1,4,7,13,16,19-hexaazacyclotetracosane.[4a] The tritosylate, a known material,[20] was isolated by column chromatogrpahy and detosylated at 95 °C with concentrated H_2SO_4 under nitrogen. The resulting colorless oil was characterized by mass spectroscopy (parent ion *m/e* 171) and its proton NMR spectrum.

Preparation of $[Cu(TCD)(NO_3)](NO_3)$. Crystals of this compound were obtained by first dissolving 0.204 g (0.88 mmol) of $Cu(NO_3)_2{\cdot}2.5H_2O$ in 10 mL of an 88 mM methanolic solution of TCD. After the resulting deep blue solution was allowed to stand for some minutes at room temperature, crystals began to deposit. They were filtered, washed with ether, and dried in a stream of air: yield of this first crop 26%; mp 205–210 °C dec. Anal. Calcd for $CuO_6N_5C_9H_{21}$: C, 30.12; H, 5.90; N, 19.52; Cu, 17.7. Found: C, 30.42; H, 5.94; N, 19.58; Cu (by atomic absorption), 18.6.

Spectroscopy. Electron spin resonance spectra were obtained at 77 K by using a Varian E-line X-band spectrometer. The spectra were recorded, digitally stored, and doubly integrated on a DEC MINC computer interfaced to the spectrometer.[21] The magnetic field was calibrated by using the Mn(II) impurity in strontium oxide.[22] UV–visible spectra were recorded on a Cary 118C spectrophotometer at 25 °C using matched quartz cells of 1-cm path length.

Electrochemistry. Cyclic voltammetry was performed under nitrogen at 20 °C with a Princeton Applied Research (PAR) Model 173 potentiostat, a Model 175 universal programmer, and an Omnigraph 2000 X-Y recorder (Houston Instruments). The working electrode was made of glassy carbon or was a platinum-bead electrode. A platinum coil served as counterelectrode. The reference electrode was a silver wire immersed in an acetonitrile solution (0.1 M $LiClO_4$ and 0.01 M $AgNO_3$). The supporting electrolyte was 0.1 M $LiClO_4$. the ferrocene/ferrocenium (Fc/Fc^+) couple[24] was used as a reference[23,24] and as a control for the stability of the system. A "blank" was run to monitor the purity of the solvent and the supporting electrolyte. Reversibility was checked by measuring the peak-to-peak separation as a function of sweep rate and by plotting i_{red} vs. the square root of the sweep rate. Voltammograms were taken of 1 mM solutions of the metal complexes.

Collection and Reduction of X-ray Data. The dark blue crystal used for the diffraction study had approximate dimensions of 0.02 mm × 0.06 mm × 0.25 mm. Its quality was checked on the diffractometer by taking open-counter ω scans of several strong low-angle reflections and was judged to be acceptable. The lattice parameters and orthorhombic crystal system obtained from studies on the diffractometer were confirmed by examining oscillation and Weissenberg

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Table II. Experimental Details of the X-ray Diffraction Study of $[Cu(TCD)(NO_3)](NO_3)$

(A) Crystal Parameters[a] at 24 °C

a, Å	14.104 (2)	space group	*Pnma*
b, Å	8.882 (3)	mol wt	358.8
c, Å	12.054 (1)	*Z*	4
V, Å^3	1510	ρ, g cm^{-3}	1.578

(B) Measurement of Intensity Data[b]

instrument: Enraf-Nonius CAD-4F κ-geometry diffractometer
radiation: Mo Kα (λ_{α_1} = 0.709 30 Å, $\lambda_{\bar{\alpha}}$ = 0.710 73 Å) graphite monochromatized
stds, measd every 1 h of X-ray exposure time (only random, statistical variations): $(\bar{2}29)$ $(32\bar{7})$ $(4\bar{5}\bar{6})$
no. of reflcns collcd: [3° ≤ 2θ ≤ 30° (+*h*, −*k*, +*l*)]; [3° ≤ 2θ ≤ 55° (+*h*, +*k*, +*l*)]
nonextinguished reflcns: 2451

(C) Treatment of Intensity Data

redn to F_o and $\sigma(F_o)$: corrn for bkgd, attenuator, and Lorentz-polarization of monochromatized X-radiation[b]
μ, cm^{-1}: 14.78
transmissn factor range[f]: 0.911–0.965
R_{av}: 0.011 (for 393 equiv pairs in the inner sphere)
no. of reflcns after averaging: 1834
no. of data used in the refinement ($F_o > 4\sigma(F_o)$): 1028

[a] From a least-squares fit of the setting angles of 25 reflections with 2θ > 34°. [b] See ref 25 for typical data collection and reduction procedures in our laboratory.

Table III. Final Positional Parameters for $[Cu(TCD)(NO_3)](NO_3)$[a]

ATOM	x	y	z
Cu	0.17362(10)	0.2500	0.01413(10)
N(1)	0.1068(8)	0.2500	0.1588(10)
N(4)	0.2129(6)	0.4618(9)	0.0511(7)
N(3)	0.0944(8)	0.2500	-0.1745(8)
N(5)	0.3656(11)	0.2500	0.3884(9)
C(2)	0.1308(10)	0.3837(13)	0.2237(11)
C(3)	0.1434(10)	0.5081(15)	0.1398(10)
C(5A)	0.2957(11)	0.480(3)	0.1247(14)
C(5B)	0.3172(10)	0.484(3)	0.060(3)
C(6A)	0.384(2)	0.344(3)	0.064(3)
C(6B)	0.3673(18)	0.4570(18)	0.0280(16)
C(7)	0.3877(13)	0.2958(18)	-0.0124(15)
O(1)	0.0390(6)	0.2500	-0.0922(7)
O(2)	0.1808(6)	0.2500	-0.1537(6)
O(3)	0.0630(7)	0.2500	-0.2701(6)
O(4)	0.2838(9)	0.2500	0.4287(10)
O(5)	0.4060(5)	0.3713(8)	0.3713(6)

[a] Numbers in parentheses are errors in the last significant digit(s). See Figure 1 for atom-labelling scheme.

Table IV. Interatomic Distances (Å) and Angles (deg) for $[Cu(TCD)(NO_3)](NO_3)$[a]

	Coordination Sphere		
Cu-N(1)	1.982(12)	Cu-O(1)	2.291(8)
Cu-N(4)	2.011(8)	Cu-O(2)	2.026(7)
N(1)-Cu-N(4)	86.3(5)	O(1)-Cu-O(2)	58.9(3)
N(4)-Cu-N(4)'	138.6(5)	O(2)-Cu-N(1)	154.5(4)
N(1)-Cu-O(1)	95.6(4)	O(2)-Cu-N(4)	102.0(3)
		N(4)-Cu-O(1)	110.6(3)
	Ligand Geometry		
C(2)-N(1)	1.462(14)	C(6B)-C(7)	1.539(23)
C(2)-C(3)	1.509(18)	C(7)-C(6A)'	1.547(34)
C(3)-N(4)	1.508(16)	C(6A)'-C(5B)'	1.557(38)
N(4)-C(5A)	1.476(19)	C(5B)'-N(4)'	1.488(17)
C(5A)-C(6B)	1.557(28)		
C(2)-N(1)-Cu	111.2(7)	C(5A)-C(6B)-C(7)	118.9(17)
C(3)-N(4)-Cu	103.5(7)	C(6B)-C(7)-C(6A)'	123.5(18)
C(5A)-N(4)-Cu	117.2(12)	C(7)-C(6A)'-C(5B)'	130.3(24)
C(2)-N(1)-C(2)'	108.7(12)	C(6A)'-C(5B)'-N(4)'	119.4(21)
N(1)-C(2)-C(3)	105.2(10)	C(5B)'-N(4)'-Cu	114.4(12)
C(2)-C(3)-N(4)	110.6(10)	C(5B)'-N(4)'-C(3)'	123.6(16)
C(3)-N(4)-C(5A)	93.3(10)		
N(4)-C(5A)-C(6B)	92.8(13)		
	Anion Geometry		
N(3)-O(1)	1.263(13)	N(5)-O(4)	1.252(19)
N(3)-O(2)	1.245(15)	N(5)-O(5)	1.236(10)
N(3)-O(3)	1.234(12)		
N(3)-O(1)-Cu	85.8(6)	O(2)-N(3)-O(3)	122.6(10)
N(3)-O(2)-Cu	95.8(6)	O(4)-N(5)-O(5)	119.3(7)
O(1)-N(3)-O(2)	116.6(9)	O(5)-N(5)-O(5)'	121.3(14)
O(1)-N(3)-O(3)	120.8(11)		
	Hydrogen Bonds		
N(4)···O(4)	2.955(10)	N(1)···O(5)	3.053(13)
N(4)···O(5)	3.116(11)		

[a] See footnote *a*, Table III. Values reported have not been corrected for thermal motion.

photographs of the crystal using Cu K$\bar{\alpha}$ radiation (λ 1.5418 Å). Further details of the data collection and reduction appear in Table II and ref 25.

Determination and Refinement of the Structure. Study on the diffractometer revealed the systematic absences 0*kl*, $k + l \neq 2n$, and *hk*0, $h \neq 2n$. These conditions are consistent either with space group *Pnma* (D_{2h}^{16}) or *Pn*2$_1$*a* (C_{2v}^{9}).[26] The structure was solved successfully in space group *Pnma*. The position of the Cu atom was located from the Patterson map. All non-hydrogen atoms remaining were found on subsequent difference Fourier maps. Neutral-atom scattering factors and anomalous dispersion corrections were obtained from ref 27.

Although the initial model obtained refined to $R_1 = 0.052$,[28] with anisotropic temperature factors and hydrogen atoms included, it had distorted bond lengths and angles and unrealistically large thermal ellipsoids for the carbon atoms. The orientation of these thermal ellipsoids indicated that the cyclic ligand was disordered across the crystallographic mirror plane at $y = {}^1/_4$. The disorder was due only to the carbon atoms, and an examination of a contoured difference Fourier map with the carbon atoms removed revealed electron density peaks elongated in the *y* direction, as expected. The disordered carbon atoms of the diethylenetriamine unit were too close to be resolved and refined as separate peaks, but the carbon atoms of the pentamethylene chain could be split and refined separately with occupancy factors of 0.5. Attempts to refine the structure in the acentric space group *Pn*2$_1$*a* produced high correlations and very unsatisfactory geometry.

The most suitable model used in the final stage of refinement constrained the N–C and C–C bond distances within the limits 1.51–1.56 Å. The pentamethylene chain was refined as two disordered forms, displaced off the mirror plane at $y = 0.25$ on alternate sides. Although this model gave reasonable anisotropic thermal parameters, the carbon atoms were refined isotropically in the final refinement cycle. Hydrogen atoms were not located in the difference Fourier map, nor were they placed in their calculated positions.

Least-squares refinement of 95 variables, using SHELX-76,[29] converged to final residual indices[28] of $R_1 = 0.080$ and R_2 0.104. The function minimized in the least squares was $\sum w(|F_o| - |F_c|)^2$, where $w = 1.9958/[\sigma^2(F_o) + 0.000625F_o^2]$. In the final refinement cycle, no parameter shifted by more than 0.003 of its estimated standard deviation. The final difference Fourier map showed no peaks greater than ~1 e Å^{-3}, the largest of which was located between carbon atoms C(2) and C(3). The average $w\Delta^2$ for groups of data showed slightly higher values at low $(\sin\theta)/\lambda$, $|h|$, $|k|$, and $|l|$, probably because hydrogen atoms, which contribute significantly to the X-ray scattering at low angles, were not included in the model.

Table III contains the final atomic positional parameters for all atoms, with their standard deviations. Table IV lists the bond distances and angles. The sizes and orientations of the thermal ellipsoids for anisotropically refined atoms are shown along with the atom-labeling scheme in Figure 1. The atomic thermal parameters and observed and calculated structure factors are available as Tables S1 and S2 (supplementary material).

Results and Discussion

Description of the Structure. The $[Cu(TCD)(NO_3)](NO_3)$ crystal structure consists of discrete Cu(II) monomers (Figure 1) connected through a loose network of hydrogen bonds across the lattice nitrate groups. The coordination geometry about

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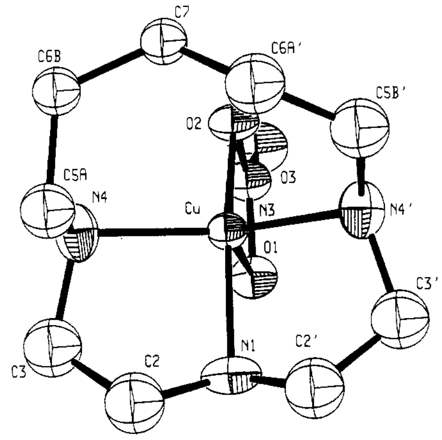

Figure 1. Structure of the $[Cu(TCD)(NO_3)]^+$ cation showing the atom-labeling scheme and 20% probability thermal ellipsoids. Primed and unprimed atoms are related by a crystallographically required mirror plane. For clarity, only one of the two disordered sets of carbon atoms of the pentamethylene linker chain is depicted.

the Cu atom is irregular and may be described as that of either a distorted square pyramid or trigonal bipyramid. In the latter description the atom O(2) is displaced from one of the axial positions toward atom O(1) in the equatorial plane by the constraining influence of the chelating nitrate ligand. The resulting O(2)–Cu–N(1) angle of 154.5 (4)° is far from the idealized value of 180°. The two remaining atoms in the equatorial plane, N(4) and N(4)′, are symmetry related by a mirror plane that runs through the coordinated nitrate group, Cu, and N(1), which is located at the other axial site of the trigonal bipyramid. The angles within the equatorial plane [N(4)–Cu–N(4)′ = 138.6 (5)°; N(4)–Cu–O(1) = 110.6 (3)°] sum up to 360°, although they are distorted from ideal values of 120° by the constraint of the minicycle. Other deviations from trigonal-bipyramidal geometry (Table IV) results from the presence of the 4- and 5-membered chelate rings.

The Cu–N bond lengths in $[Cu(TCD)(NO_3)](NO_3)$ are inequivalent, as found for most (but not all[31]) other complexes containing a chelating diethylenetriamine fragment,[2,3,30] The two Cu–O distances are also markedly inequivalent. A similar difference occurs in (oxalato)(diethylenetriamine)copper(II) tetrahydrate,[31] where the Cu–O bonds of the copper oxalate chelate ring are 2.230 (6) and 1.965 (6) Å. In both structures the longer Cu–O distance involves the bond to the apical ligand in a square-pyramidal description of the structure, a common feature for this stereochemistry. The copper atom in $[Cu(TCD)(NO_3)](NO_3)$ is situated 0.70 Å from the plane defined by the three nitrogen donor atoms of the TCD ligand. For the complexes $Cu([9]aneN_3)Cl_2$[15] and $Cu([9]aneN_3)Br_2$[16] the corresponding values are 1.37 and 1.36 Å, respectively. Since the smaller minicycle enforces facial coordination on the triaza copper(II) fragment, these latter two complexes have square-pyramidal structures.

Although the disorder found in the crystal limits the accuracy with which the geometry of the pentamethylene chain can be determined, the bond angles in Table IV reveal substantial strain. The coordinated and free nitrate groups show no unusual features.

Redox Behavior. Cyclic voltammograms of the ferrocene/ferrocenium (Fc/Fc^+) couple exhibit reversible electrochemical behavior in 0.1 M $LiClO_4$/acetonitrile solutions. An average peak-to-peak separation (ΔE_p) of 59–63 mV is observed for scan rates between 10 and 200 mV s^{-1}, depending upon the electrode used. Solutions of $[Cu(TCD)(NO_3)](NO_3)$ show quasi-reversible voltammograms (Figure 2) under these conditions. Both E_p and the shape of the wave depend upon the electrode used and the prior treatment of its surface. With the platinum electrode a peak-to-peak separation of 60 mV is observed, the complex having an $E_{1/2}$ of −185 mV relative to Fc/Fc^+. By contrast, $[Cu(dien)(NO_3)](NO_3)$ shows only a reduction wave (Figure 2), the shape of which indicates an irreversible electrode reaction (previous work[21] on related compounds revealed more reversible cyclic voltammograms at the glassy-carbon electrode). $[Cu(dien)]^+$ is reduced at a potential of −450 mV relative to Fc/Fc^+. Thus, by restricting the flexibility of the dien ligand through the introduction of a pentamethylene chain, the respective Cu(II) complex is reduced at a potential 265 mV more positive.

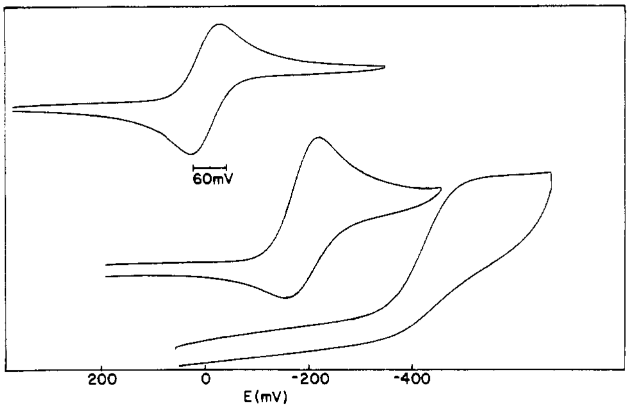

Figure 2. Cyclic voltammograms of ferrocene/ferrocenium ion, Fc/Fc^+ (top), $[Cu(TCD)(NO_3)](NO_3)$ (middle), and $[Cu(dien)(NO_3)](NO_3)$ (bottom) in acetonitrile. The scan rate was 100 mV s^{-1}; other experimental details are given in the text. Potentials are referenced to Fc/Fc^+.

Table V. Visible Spectral Parameters for 3 mM Aqueous Solutions of $[Cu(TCD)(NO_3)](NO_3)$

pH	buffer or additive	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}
6.2	none	660	80
11.1	2 equiv of NaOH	630	87
8.9	0.1 M borate	660	70
11.3	0.2 M phosphate	675	70

In a study of neutral four-coordinate Cu(II) chelates with salicylaldimine and related ligands, it was shown that nonplanar bis-chelate complexes are easier to reduce than their planar analogues, rigid planar tetradentate or planar bis-chelate complexes. Positive potential shifts were observed when destabilization of planar Cu(II) and/or stabilization of nonplanar Cu(I) was achieved by sterically constraining the ligand. In the case of $[Cu(TCD)]^+$ the rigid ligand not only demands that the Cu(II) be displaced 0.7 Å from the plane defined by the three nitrogen donors but also, by its $(CH_2)_5$ backbone, prevents the metal ion from reaching its favored tetragonal coordination geometry. In particular, the N(4)–Cu–N(4)′ angle cannot become much larger than 138°, as would be required for a square-pyramidal stereochemistry with the "dien" portion of the macrocycle in the basal positions. This steric constraint must be responsible for the shifts in redox potential and of the ligand field transition (vide infra). Although the cuprous state is more favored by TCD than by dien, an aerobic solution of $[Cu(TCD)]^+$ in acetonitrile remains colorless only under a positive pressure of carbon monoxide; otherwise an irreversible autoxidation occurs.

Solution Spectroscopy and Chemistry. Solutions of $[Cu(TCD)(NO_3)](NO_3)$ show one absorption in the ligand field region, which is dependent on pH and buffers (Table V).

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[30] Stephens, F. S. *J. Chem. Soc. A*. **1969**, 2233.
[31] Stephens, F. S. *J. Chem. Soc. A* **1969**, 2493.
[32] Patterson, G. S.; Holm, R. H. *Bioinorg. Chem.* **1975**, *4*, 257.
[33] Cf.: Pasquali, M.; Marchetti, F.; Floriani, C. *Inorg. Chem.* **1978**, *17*, 1684.

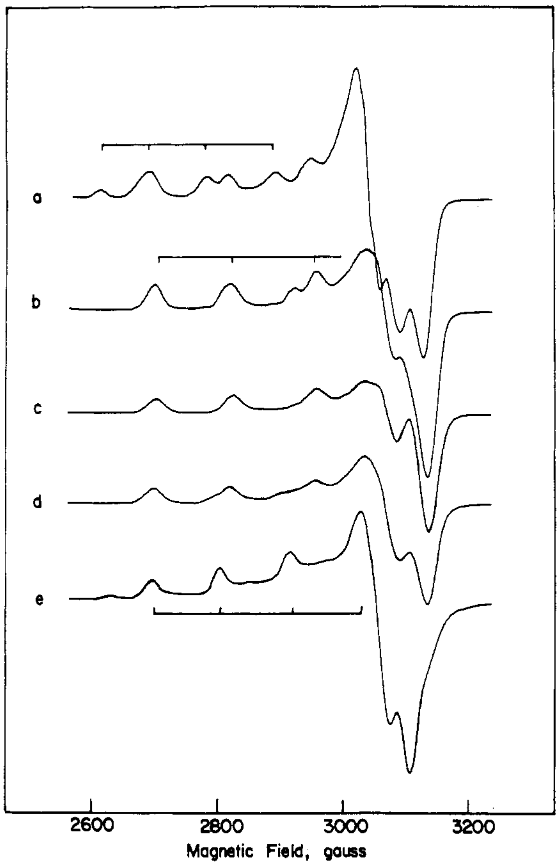

Figure 3. ESR spectra of 8 mM frozen (77 K) 50% aqueous dimethyl sulfoxide solutions of $[Cu(TCD)(NO_3)](NO_3)$: (a) at pH 6.2; (b) at pH 11.1; (c) at pH 8.5; (d) in borate buffer at pH 8.9; (e) in phosphate buffer at pH 11.3. Instrumental settings: microwave power 10 mW; modulation amplitude 5 G; time constant 0.3 s; sweep rate 500 G m^{-1}.

Table VI. Electron Spin Resonance Parameters of 50% Aqueous Dimethyl Sulfoxide Solutions of $[Cu(TCD)(NO_3)](NO_3)$ at 77 K[a]

conditions	$g_\parallel$	$A_\parallel$, G	$A_\parallel$, $cm^{-1} \times 10^4$	$g_\perp$
	2.392, 2.35	118, 176	132, 184	2.075, 2.046
pH 8.5	2.235	169	176	2.049[b]
pH 11.1	2.228	167	174	2.044[b]
pH 8.9; 0.1 M borate	2.228	176	183	2.046[b]
pH 11.3; 0.2 M phosphate	2.263	153	162	2.058[b]
$+2CN^-$	2.175	184	186	2.041
Cu^{2+}, no TCD	2.404	114	128	2.077

[a] The pH reported was measured before addition of dimethyl sulfoxide. See also the caption to Figure 3. [b] The second feature in this region (Figure 3) may indicate rhombic symmetry.

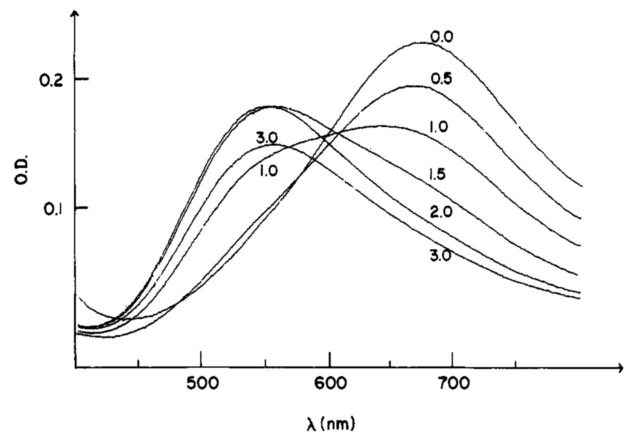

Figure 4. Visible spectra of a 3.2 mM solution of $[Cu(TCD)(NO_3)](NO_3)$ in 0.2 M phosphate at pH 11.3 as a function of added equivalents of cyanide ion. The CN^-/Cu ratio is given.

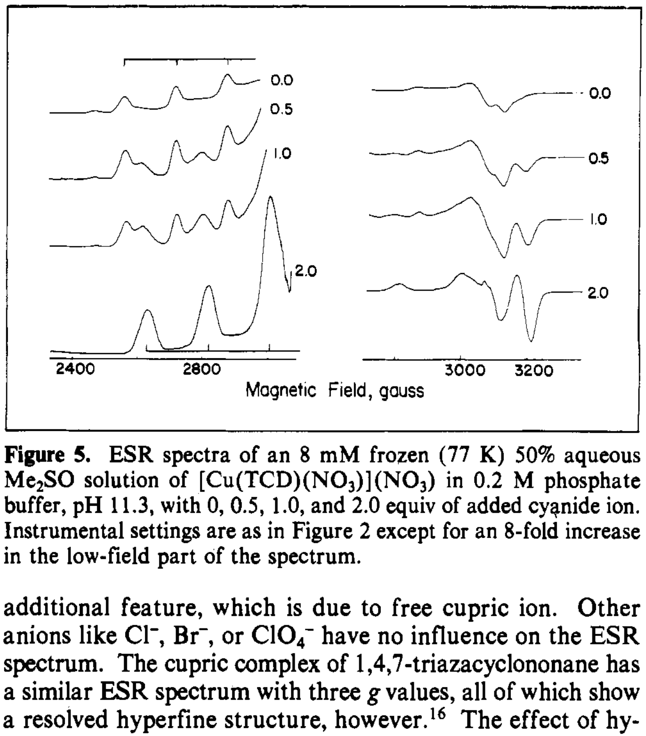

Figure 5. ESR spectra of an 8 mM frozen (77 K) 50% aqueous Me_2SO solution of $[Cu(TCD)(NO_3)](NO_3)$ in 0.2 M phosphate buffer, pH 11.3, with 0, 0.5, 1.0, and 2.0 equiv of added cyanide ion. Instrumental settings are as in Figure 2 except for an 8-fold increase in the low-field part of the spectrum.

Increasing pH results in a shift of the maximum toward shorter wavelengths, analogous to the cupric complexes of dien, 1,4,7-triazacyclodecane, and 1,5,9-triazacyclododecane (Table I). The complex of TCD absorbs at a longer wavelength than that of dien, as do the other triaza macrocycles listed in Table I. The visible spectrum of $Cu(TCD)^{2+}$ is typical for Cu(II) in a pseudotetragonal ligand field and not for pseudotetrahedral or trigonal symmetry. This result strongly indicates that the coordinated nitrate ligand is replaced by water. Pseudotetragonal symmetry is further indicated by the ESR spectra, which show the typical, nearly axial Cu(II) pattern (Figure 3). In borate and phosphate buffers, or in the presence of base, there is one major species in the $g_\parallel$ region (Table VI). The $Cu(TCD)^{2+}$ cation at pH 6.2 shows an additional feature, which is due to free cupric ion. Other anions like Cl^-, Br^-, or ClO_4^- have no influence on the ESR spectrum. The cupric complex of 1,4,7-triazacyclononane has a similar ESR spectrum with three g values, all of which show a resolved hyperfine structure, however.[16] The effect of hydroxide and phosphate both on the visible and the ESR spectra shows that these ligands coordinate, presumably achieving pseudotetragonal symmetry. A red shift upon the coordination of OH^- is also observed with the cupric complexes of other triaza macrocycles (Table I) and with dien, where hydroxide coordinates in the plane of the nitrogen atoms.

Addition of 2 equiv of CN^- ion results in a 120-nm blue shift of the d–d band (Figure 4). In borate and phosphate buffers, where pH effects are minimized, this shift progresses with the number of equivalents of added cyanide until 2 are present. Additional CN^- results in a slight reversal of the shift and in reduction[34] of Cu(II), as seen by the disappearance of the visible band. For the $Cu(TCD)^{2+}/2CN^-$ system these results could mean that pseudotetragonal coordination is achieved by attachment of two cyanides and two of the amines of the minicycle, with the third one being uncoordinated or only weakly bound. The alternative interpretation of one CN^- coordinating weakly in an apical position seems less likely because in this case one would expect to see the spectral shift maximized upon the addition of one cyanide ligand. In $[PdCl_2(TCDH)](ClO_4)\cdot H_2O$, one nitrogen atom of the minicycle

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(34) Billo, E. J. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 673.

is similarly believed to be uncoordinated.[35]

This interpretation is supported by the ESR spectrum (Figure 5), which shows the formation of a new complex of axial symmetry (Table VI). A decrease of $g_\parallel$ and an increase in $A_\parallel$ are to be expected if the charge on the complex decreases.[36] For Cu(TCD)$^{2+}$ the changes in $g_\parallel$ from 2.263 to 2.175 and in $A_\parallel$ from 162 to 186 G are the ones anticipated for a charge decrease of 2 units. Both the ESR and optical spectra indicate that, with less than 2 equiv of added cyanide ion, a mixture of Cu(TCD)$^{2+}$ and the cyano complex is present. Thus, a dicyano complex forms preferentially with no significant amount of an intermediate monocyano species.

With Cu(dien)$^{2+}$, a shift from 620 to 550 nm occurs upon the addition of 1 equiv of CN$^-$. The second equivalent shifts the d-d band back to 625 nm, and spontaneous reduction occurs.[34] The blue shift upon the addition of one cyanide indicates coordination in the basal plane, and the subsequent shift reversal is consistent with apical binding,[34] a well-known phenomenon for copper(II) amine complexes.[17]

Relevance to the Chemistry of Copper Protein Active Sites. Connecting the terminal nitrogen atoms of the diethylenetriamine ligand with a pentamethylene chain produces several important consequences for its 1:1 copper(II) complex. Owing to the constrained N-Cu-N angle of 138.7°, it is easier to reduce Cu(TCD)$^{2+}$ than Cu(dien)$^{2+}$ and the electrochemical redox reaction is more reversible. Both high redox potentials and reversible redox behavior are features characteristic of copper centers in biology,[37] and the present study demonstrates how the protein environment might use stereochemistry to tune a CuN$_3$ center to achieve these characteristics. It is interesting, moreover, that Cu(TCD)$^{2+}$ takes up two cyanide ligands into its principal coordination plane, presumably with loss of one of the amine donor atoms of the TCD minicycle and relief of the steric constraint, compared with Cu(dien)$^{2+}$ which only binds one CN$^-$ ligand in the basal plane. These results may be compared with those for met apo hemocyanin.[38] Here the so-called "endogenous" ligand is tightly bound to copper, and only one cyanide ion coordinates strongly. A second such ligand binds only in the presence of 100-fold excess cyanide, presumbly in an apical position. Thus, Cu(dien)$^{2+}$ more closely mimics the copper site in this protein derivative than does Cu(TCD)$^{2+}$. Had met apo hemocyanin bound tightly to two cyanide ligands, however, this information could not have been used to argue that two in-plane sites were unoccupied by a strong donor ligand (e.g., histidine), as the present results demonstrate.

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Registry No. [Cu(TCD)(NO$_3$)](NO$_3$), 90790-08-2; [Cu(dien)(NO$_3$)](NO$_3$), 90790-10-6; Cu(TCD)$^{2+}$, 90790-11-7; Cu(dien)$^{2+}$, 45520-77-2; Cu(TCD)$^{2+}$/2CN$^-$, 90790-12-8.

Supplementary Material Available: Listings of atomic thermal parameters and observed and calculated structure factors (Tables S1 and S2) for [Cu(TCD)(NO$_3$)](NO$_3$) (6 pages). Ordering information is given on any current masthead page.

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(36) Peisach, J.; Blumberg, W. E. *Arch. Biochem. Biophys.* **1974**, *165*, 691.

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Contribution from the Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, 50132 Firenze, Italy, and Istituto Ricerca Onde Elettromagnetiche, CNR, 50127 Firenze, Italy

Low-Temperature Crystal Structure of a Five-Coordinate Iron(II) Complex Exhibiting Singlet-Triplet Spin Equilibrium

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The [Fe(P$_4$)Br]BPh$_4$·CH$_2$Cl$_2$ complex (P$_4$ = hexaphenyl-1,4,7,10-tetraphosphadecane) shows a smooth variation of the magnetic moment between 86 K (μ_{eff} = 0.89 μ_B) and 376 K (μ_{eff} = 2.26 μ_B) and is a rare example of singlet-triplet equilibrium in iron(II) complexes. At room temperature this compound has an intermediate-spin state (μ_{eff} = 1.60 μ_B), and its structural parameters have been previously reported. The crystal and molecular structure at 150 K has been determined in order to detect the structural changes associated with the spin transition. The space group does not change on cooling. Crystal data: C$_{67}$H$_{64}$BBrCl$_2$FeP$_4$, triclinic system, space group $P\bar{1}$, a = 13.549 (9) Å, b = 19.058 (12) Å, c = 12.475 (8) Å, α = 72.0 (1)°, β = 82.4 (1)°, γ = 81.2 (1)°, Z = 2. The structure was refined by full-matrix least-squares methods to the conventional R factor value of 0.079 for 3500 observed reflections. The variation in the cell parameters is accompanied by significant decrease in distortions from the idealized C_{2v} symmetry. Angular-overlap model calculations well account for the smooth variation of the magnetic moment and support the hypothesis that the spin equilibrium is due to a general increase of the mean ligand field by decreasing temperature.

Introduction

Depending upon the strength of the ligand field (LF), high-spin or low-spin ground states can occur in octahedral transition-metal complexes having electronic configurations d^4, d^5, d^6, and d^7. When the restriction of O_h symmetry is released, ground states of different spin multipicities are theoretically allowed also for electronic configurations d^2, d^3, and d^8. For intermediate LF's an anomalous magnetic behavior is observed, which often has been named spin crossover or spin equilibrium.

By now many examples of such a phenomenon have been described,[2,3] particularly in the chemistry of iron(II), iron(III),

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(1) (a) Istituto Stereochimica. (b) Istituto Onde Elettromagnetiche.

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