give a measure of $\delta E(\text{e–b}_2)$ and $\Delta E(\text{b}_1\text{–b}_2)$. The results obtained for vanadium and niobium compounds are given in Table II. (3) The A values increase progressively from V to Ta. This variation does not seem to be related to the dipolar part of the hyperfine coupling, the anisotropic components ($A_{\parallel} - A_{\text{iso}}$) and ($A_{\perp} - A_{\text{iso}}$) being almost constant throughout the series, but seems to be rather due to the Fermi contact term which increases when going down the periodic table.[7] It is also possible to determine the correct signs of the A parameters using the analysis of Fortman.[8] The unpaired electron is in an orbital perpendicular to the symmetry axis and the nuclear magnetic moment is positive for the three elements ^{51}V, ^{91}Nb, and ^{181}Ta; it follows that the anisotropic splitting component A_{p} is negative.[9] The isotropic splitting A_{iso} is negative also since the nuclear magnetic moment is positive and also because the 4s contribution to the hyperfine splitting is small due to nonmixing with the 4s and the d_{xy} orbitals. With the experimental A values (see Table I) and the relationship $A_{\text{iso}} = {}^1/_3(A_{\parallel} + 2A_{\perp})$, $A_{\parallel}$, $A_{\perp}$, and A_{iso} are all of the same sign, and from the above results they are all negative for the three compounds ($A_{\parallel} = 2A_{\text{p}} + A_{\text{iso}}$ and $A_{\perp} = A_{\text{iso}} - A_{\text{p}}$). (4) The line width of the solution ESR spectra increases considerably from vanadium to tantalum (20, 60, and 70 G for V, Nb, and Ta, respectively). This could be due to a nonresolved quadrupole coupling which is particularly large in tantalum, the quadrupole moment being 10 times larger than that for vanadium and niobium. An additional factor is the increase in the molecular volume when going down the series, the molecular tumbling correlation time being dependent on the molecular size of the complex. Another interesting observation is that the line width variation with M_{I} within the same spectrum does not follow the same behavior in the three complexes. For vanadium the broader line lies on the high-field side of the spectrum, whereas the reverse effect is observed for niobium and tantalum.

According to Kivelson,[10,11] the line width $1/T^2$ in the case of rapid tumbling is related to the nuclear spin parameter number by the relation

$$1/T^2 = \frac{\tau_{\text{c}}(g_{\text{b}}\beta H + bM_{\text{I}})^2}{\hbar^2} \tag{1}$$

where τ_{c} is the correlation time of the molecular tumbling, $g_{\text{b}} = {}^1/_3(g_{\parallel} - g_{\perp})$ and $b = {}^1/_3(A_{\parallel} - A_{\perp})$. The smaller line width should occur for that value of M_{I} which minimizes the expression within the parentheses in eq 1. The main difference between the three compounds arises from the fact that for vanadium g_{b} is negative while it is positive for niobium and tantalum. This may account for the difference observed in the variation of line width with M_{I}.

A well-resolved superhyperfine structure is observed on the ESR spectra of the vanadium compound, showing that the 3d electron is interacting with two equivalent phosphorus nuclei. This hyperfine splitting is less neatly resolved in the case of niobium, and for tantalum it is only visible on the frozen solution spectrum. This of course is due to line width variation which increases down the series.

The superhyperfine coupling parameters (a) for the three compounds keep a virtually constant value throughout the series and are almost isotropic, showing that they mainly involve "s" orbital electron density. They are also rather low, showing weak interaction of the unpaired electron with phosphorus.

An electron transfer from the d_{xy} metal orbital toward the "σ" phosphorus orbital cannot account for the observed superhyperfine coupling. It would be forbidden anyway by symmetry considerations, the "σ" orbitals being orthogonal to the $\text{b}_{2\text{g}}$ molecular orbitals. A spin polarization of the "σ" doublet by the unpaired 3d electron would give a more satisfactory model for the superhyperfine coupling mechanism.

The reactions of these tetrahalides with other phosphines of varying basicity and correlation of this basicity with the ESR parameters will be described in a forthcoming publication.

Registry No. VCl_4, 7632-51-1; $NbCl_4$, 13569-70-5; $TaCl_4$, 13569-72-7; $VCl_4\cdot 2PEt_3$, 73079-35-3; $NbCl_4\cdot 2PEt_3$, 73135-97-4; $TaCl_4\cdot 2PEt_3$, 73079-36-4.

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Redox Behavior of a Dinuclear Copper Cryptate: A Dielectronic Receptor Site

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Several recent papers[2–5] have been devoted to the analysis of the redox behavior of dinuclear copper(II) complexes, in the hope to clarify or to replicate the oxido-reductive function of copper proteins. Depending upon the ligand, the reduction into the corresponding Cu(I) complexes occurs via two successive and distinct monoelectronic steps[2a,4,5] or in a unique dielectronic step involving two monoelectronic transfers of identical standard potential.[2b,3] This last system[2b,3] is the only example known up to now in which a dinuclear Cu(II) complex is reversibly reduced to the corresponding dinuclear Cu(I) species by two monoelectronic steps which are simultaneous on the macroscopic time scale of the electrochemical measurements (i.e., identical values of $E_{1/2}$). However, with one exception,[5] all the above complexes involve oxygen-bridged Cu(II) cations. Thus,.the two Cu(II) are not structurally independent, and it is therefore not surprising that the two $E_{1/2}$ potentials, corresponding to their successive reductions to the dinuclear species (Cu(II), Cu(I)) and (Cu(I), Cu(II)), differ by values ranging from 0[2b,3] to several tens or hundreds of millivolts[2a,4,5] depending on the ligand. Furthermore these complexes[2–5] exhibit standard redox potentials E_0 at least 600 mV more negative than the standard redox potentials characterizing the copper proteins.[6]

The synthesis and the properties of a new macrocyclic ligand and of its Cu(II) dinuclear complex,[7] as well as its structure,[8] have been recently reported. Complexation of Cu(II) by this macrotricyclic ligand (1,7,13,19-tetraaza-4,16-dioxa-

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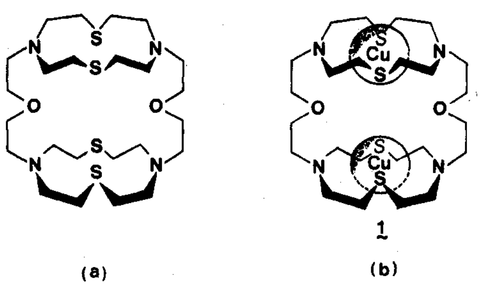

Figure 1. Cylindrical macrotricyclic ligand (a) and corresponding dinuclear Cu(II) complex **1** (b).

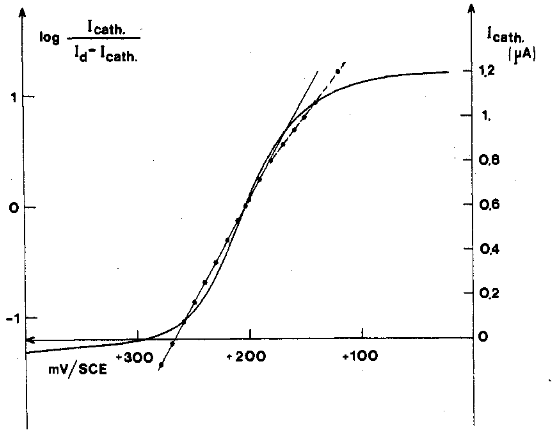

Figure 2. Reduction of dinuclear Cu(II) complex **1** on Pt RDE (250 rev min^{-1}; H_2O + 0.1 M KCl; 2 mV s^{-1}; [complex **1**] = 1.30×10^{-4} M).

10,22,27,32-tetrathiatricyclo[17.5.5.$5^{7,13}$]tetratriacontane) (Figure 1a)[7] produces a stable dinuclear Cu(II) cryptate (complex 1, Figure 1b) whose chemical and structural characteristics (S heteroatoms, flexibility of the ligand, relative position of the two coppers, and two identical coordination sites for the two coppers) lead one to expect unusual redox properties. In particular, the distorted coordination of Cu in complex **1**[8] may favor the conversion of Cu(II) to Cu(I).

The electrochemical behavior of complex **1** has been studied in H_2O + 0.1 M KCl,[9] on Pt electrodes, by voltammetry on a rotating disk electrode (RDE) and by cyclic voltammetry. On RDE, a two-electron, diffusion-controlled, cathodic wave is observed at $E_{1/2} = +200 \pm 5$ mV/SCE (Figure 2). The diffusion coefficient calculated from Levich's relationship[11] is $D = (3.7 \pm 0.2) \times 10^{-6}$ cm^2 s^{-1}. The slope of the logarithmic analysis of the wave is 57 ± 2 mV (Figure 2) with, however, a higher value than 57 mV for the top of the stationary wave, which corresponds to a quasi-reversible reduction as confirmed hereafter from cyclic voltammetry. Coulometric reductions confirm that 2 Faradays are exchanged per mole of complex **1**. Also, during the coulometry, the initial violet solution becomes colorless, and the electronic spectra recorded on the reduced solution reveal the absence of absorption bands between 350 and 760 nm, as expected for a Cu(I) complex. In cyclic voltammetry, complex **1** exhibits one cathodic and one anodic peak (Figure 3) separated by $\Delta E_p = 60$ mV as long as $v < 0.2$ V s^{-1}, which is consistent with a fast ("reversible") monoelectronic electron transfer. The peaks separation ΔE_p increases with the scan rate v, and an appropriate analysis[12] of this variation gives $k_s = (1.3 \pm 0.2) \times 10^{-2}$ cm s^{-1} as the reduction rate constant at the standard redox potential. Also, the reduction peak current is proportional to $v^{1/2}$, and the cathodic and anodic peaks currents are equal at all scan rates between 0.01 and 20 V s^{-1}.

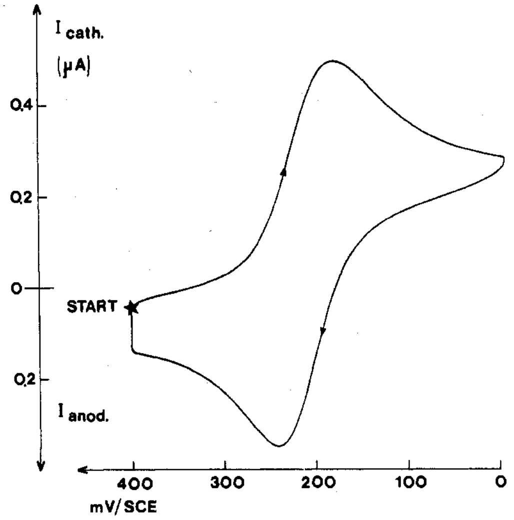

Figure 3. Cyclic voltammetry of dinuclear Cu(II) complex **1** on a Pt electrode (H_2O + 0.1 M KCl; 10 mV s^{-1}).

On the other hand, the value of the measured cathodic peak current is twice the calculated value corresponding to the hypothetical mononuclear form of complex **1** (one copper per ligand) at the same concentration. This is at significant variance with what would be observed in a reduction involving two separate mononuclear complexes.[13,14]

All the above results may be rationalized by assuming that the two redox centers (Cu(II)) are equivalent and almost noninteracting in cryptate **1**; their redox reactivity is therefore identical. In terms of redox behavior, such a situation has been recently studied, both theoretically and experimentally in the case of simultaneous (on the time scale of experiments) reduction of several independent redox centers.[13-18]

However, this is apparently the first complex in which the following characteristics are simultaneously met: (1) no bridging covalent group between the two cations, but, instead, a unique stable ligand affording two identical coordination sites to the two cations, (2) reversible monoelectronic reduction of each cation (by stationary electrochemical methods), and (3) simultaneous reduction of each cation (on the time scale of the voltammetry).

Two arguments may be adduced in favor of an almost identical reactivity of the two Cu(II) and hence of a very weak interaction between the two copper cations in dinuclear complex **1**.

The first argument results from the structure of complex **1**,[8] where the Cu(II)–Cu(II) distance is 5.62 Å. The corresponding EPR spectrum (four bands separated by 85–90 G at 9648.2 MHz in aqueous solution at 25 °C) confirms the absence of strong coupling between the two Cu(II), in agreement with previous results on the solid.[8] However these results do not disagree with the existence of a weak coupling,

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(9) The thermodynamic stability of complex **1** is high enough in H_2O (S. A. Sullivan and J. M. Lehn, unpublished research) to prevent the formation of complexes between copper and chloride ions.[10]

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as already suspected from solid-state EPR measurements.[8] Recent calculations[19] of the Cu(I)–Cu(I) interactions in a polynuclear complex demonstrate that, when the orbitals s, p, and d of each of the two Cu(I) are considered, the positive (i.e., attractive) mutual interaction of the coppers almost vanishes as soon as their distance exceeds 3.5–4 Å. It is therefore reasonable to expect the Cu(I)–Cu(I) interactions to be weak in the reduced form of **1**.

The second argument may support the occurrence of a very weak coupling between the two Cu(II) in **1**. This results from the shape of the cyclic voltammograms and from the analysis of the stationary reduction wave on a platinum rotating disk electrode. Several years ago, the theoretical analysis of the peaks in cyclic voltammetry has been developed[20] for two fast, monoelectronic, simultaneous or quasi-simultaneous reduction steps; when the redox step is neither unique nor really bielectronic (i.e., $E_2^\circ - E_1^\circ$ being not > 0), then the difference between the peak and the half-peak reduction potentials ($E_p - E_{p/2}$) exceeds 29 mV. In dinuclear complex **1** this difference is 51 ± 2 mV, which corresponds[20] to a difference $E_2^f - E_1^f = -27 \pm 3$ mV between the formal redox potentials of the two coppers (E_2^f corresponds to the second monoelectronic step). With totally uncoupled Cu(II) centers in the complex, this difference $E_2^f - E_1^f$ would be −35.6 mV at 298 K.[13,14] These cyclic voltammetry results are complemented by the slope (57 ± 2 mV) of the log plot (Figure 2) of the cathodic wave recorded on a rotating disk electrode; the reduction is fast on the time scale of the measurements, the slope 57 ± 2 mV being almost that expected[14] for a process involving two independently reduced redox centers (59.1 mV). With this value of 57 ± 2 mV, the calculated[13] difference $E_1^f - E_2^f$ is equal to 32 ± 4 mV, in agreement with the value 27 ± 3 obtained above from cyclic voltammograms. Thus, the experimental value of $E_1^f - E_2^f$ may be given as 30 ± 6 mV,[21] which is close to the 35.6 mV corresponding to the absence of interactions between the two coppers, taking into account the uncertainty of the potential measurements.

The present results are fully consistent with the reduction of the two copper(II) in cryptate **1** via two monoelectronic steps, each step involving a distinct Cu(II) center. Thus $E_0 = +200 \pm 11$ mV/SCE for each of the two Cu(II)/Cu(I) couples in **1**, the two Cu(II) being almost noninteracting.

Thus, dinuclear cryptate **1** may be considered as a *dielectronic receptor* unit, which might be able to exchange two electrons in a single encounter. It represents a prototype for the study of cooperativity between two (or more) sites in electron-transfer processes and for catalysis of reactions requiring the transfer of several electrons. Furthermore the redox properties of the dinuclear complex **1** (markedly positive standard potential and fast two-electron acceptor/donor system) mimic type 3 copper sites in copper proteins.[6]

Apart from the known effect of the macrocyclic ligand to weaken the interaction of the coppers with the surrounding medium, the unusual redox properties of complex **1** may be ascribed to the following factors: (i) The moderately positive potentials (compared to polythiamacrocycles[7,23]) arise from the chemical nature of the coordination sites (two nitrogen and only two sulfurs) as well as from the coordination stereochemistry which is intermediate between square planar and tetrahedral.[8] (ii) The ability of the cryptate to function as a "cascade-like" two-electron-transfer site results from the intercationic distance imposed by the structure of the ligand.[24]

Modifying the length of the side-branches which connect the two monocycles in the macrotricyclic ligand (Figure 1a) does not affect[25] qualitatively the general redox behavior of the dinuclear copper complex, provided their length remains large enough to prevent significant coupling between the two coppers.

Registry No. **1**, 67340-45-8; **1**, reduced form, 72925-69-0.

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(21) With the assumption of equal (fast) rate constants for the two monoelectronic steps, this difference corresponds[22] to a thermodynamic dismutation constant K of about 0.3 for the mixed complex (Cu(II),Cu(I)). [K = (2Cu^{II} ligand)(2Cu^{I} ligand)/(Cu^{II},Cu^{I} ligand)^2].

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(24) The opening of one of the side-branches in the cryptand (Figure 1a), as it suppresses this structural control, should allow various conformations. In such dinuclear copper complexes, the above results lead one to expect qualitatively analogous redox behavior with, however, a probable slowdown of the overall rate of the two-electron transfer.[22]

(25) J. P. Gisselbrecht and M. Gross, to be submitted for publication.

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Photoelectron Spectra of Nitrosyldicarbonyl(η^5-cyclopentadienyl)chromium and Thionitrosyldicarbonyl(η^5-cyclopentadienyl)chromium. Comparison of the Electronic Structures of Metal–NO and Metal–NS Complexes

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Legzdins and Kolthammer recently reported the preparation and structure of the first organometallic thionitrosyl complex, $(\eta^5\text{-}C_5H_5)Cr(CO)_2NS$ (I).[1,2] This complex is isoelectronic and basically isostructural with a large group of $(\eta^5\text{-}C_5H_5)M(CO)_2L$ complexes, where L is a small molecule or fragment species. We have found that such complexes are highly useful for providing detailed information on the relative bonding and electronic interactions between the metal and the attached ligand.[3–6] Our approach combines high-resolution study of the valence ionizations of the complex in the gas phase with appropriate theoretical calculations. It is useful to compare the thionitrosyl complex with the corresponding nitrosyl complex, $(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$ (II), and the isoelectronic and basically isostructural manganese carbonyl and thiocarbonyl complexes, $(\eta^5\text{-}C_5H_5)Mn(CO)_2CS$ (III) and $(\eta^5\text{-}C_5H_5)Mn(CO)$ (IV). It follows from the results of our similar study on complexes III and IV[4] that NS should be a better π-accepting ligand than NO, which is interesting since NO is already considered to be a strong π acid. Another very important feature should be the greater interaction of the filled NS orbitals with the metal electrons.

The nitrosyl[7] and thionitrosyl[1] complexes were prepared and purified by published procedures. Spectra were measured on a McPherson ESCA 36 spectrometer fitted with the He I source chamber and a temperature-controlled sample ionization chamber of our own design (I, 25 °C; II, 45 °C). Dis-

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