chemical parameters for Tc provide estimates of the reduction potentials of the putative aqua ions, $[Tc(H_2O)_6]^{n+}$ (n = 2-4), in *organic* media (see Table VI). These provide an indication of the *thermodynamic* stabilities of these ions, which suggest that (1) $[Tc(H_2O)_6]^+$ is probably unstable in any protic media, (2) $[Tc(H_2O)_6]^{2+}$ and $[Tc(H_2O)_6]^{3+}$ may be observable under inert atmosphere, and (3) $[Tc(H_2O)_6]^{4+}$ may be attainable in highly acidic media at Tc concentrations sufficiently low to inhibit polynuclear formation.

The synthetic reactions, steric effects, and electrochemical parameters quantified here confirm that the chemistry of technetium is somewhat more pliable than that of other transition metals. While its central position in the periodic table is often invoked as an explanation for this, the fundamentals of this question remain to be answered at the electronic level.

Supplementary Material Available: For *mer*-[Cl₃(pic)₃Tc] and *mer*-[Cl₃(pic)(PMe₂Ph)₂Tc], tables of positions for all atoms, temperature factors for non-hydrogen atoms, bond distances and angles, least-squares planes, and electrochemical data (19 pages); listing of calculated and observed structure factor amplitudes (49 pages). Ordering information given on any current masthead page.

Synthesis and Spectroscopy of Copper(II) Compounds of a Chelating Imidazole–Thioether Ligand. Molecular Structures of (1,5-Bis(4-imidazolyl)-3-thiapentane)dichlorocopper(II), (1,5-Bis(4-imidazolyl)-3-thiapentane)bis(thiocyanato-*N*)copper(II), and Bis[(*μ*-chloro)(1,5-bis(4-imidazolyl)-3-thiapentane)copper(II)] Bis(perchlorate)

M. Zoeteman,[1a] E. Bouwman,[1a] R. A. G. de Graaff,[1a] W. L. Driessen,*[1a] J. Reedijk,[1a] and P. Zanello[1b]

The synthesis and characterization of copper coordination compounds with the novel tridentate ligand 1,5-bis(4-imidazolyl)-3-thiapentane (abbreviated as bimtp) are described. The compounds are of the general formula [Cu(bimtp)X₂] with X⁻ = Cl⁻, Br⁻, NO₃⁻, and NCS⁻. Also, compounds with mixed anions were isolated with general formula [Cu(bimtp)X]Y with X⁻ = Cl⁻ and Y⁻ = ClO₄⁻ and BF₄⁻. bimtp acts as a tridentate ligand in all compounds, both imidazole nitrogens and the thioether sulfur participating in the coordination of copper. All compounds of the formula [Cu(bimtp)X₂] are five-coordinated in a distorted trigonal-bipyramidal or distorted square-pyramidal geometry. In the chloro-bridged dimer [Cu(bimtp)Cl]₂(ClO₄)₂, the copper ion is five-coordinated in a square pyramid. Single crystals of [Cu(bimtp)Cl₂], [Cu(bimtp)(NCS)₂], and [Cu(bimtp)Cl]₂(ClO₄)₂ were used for structure determinations, using heavy-atom techniques and refined by least-squares methods. [Cu(bimtp)Cl₂]: orthorhombic, space group $P2_12_12_1$, a = 7.605 (2) Å, b = 8.280 (1) Å, c = 22.644 (5) Å, Z = 4, T = 293 K; R = 0.032, R_w = 0.040 for 1605 reflections; Cu–N = 1.97 Å, Cu–Cl = 2.48 and 2.32 Å, Cu–S = 2.50 Å, in an almost ideal trigonal-bipyramidal geometry. [Cu(bimtp)(NCS)₂]: monoclinic, space group $P2_1/n$, a = 13.000 (2) Å, b = 16.400 (3) Å, c = 8.131 (1) Å, $β$ = 105.9 (1)°, Z = 4, T = 293 K; R = 0.045, R_w = 0.047 for 3035 reflections; Cu–N = 1.96 and 1.98 Å, Cu–NCS = 1.99 and 2.00 Å, Cu–S = 2.60 Å, in a distorted trigonal-bipyramidal geometry. [Cu(bimtp)Cl]₂(ClO₄)₂: monoclinic, space group $P2_1/c$, a = 8.703 (2) Å, b = 13.776 (3) Å, c = 12.857 (2) Å, $β$ = 97.47 (2)°, Z = 2, T = 293 K; R = 0.046, R_w = 0.057 for 3151 reflections; Cu–N = 1.95 Å, Cu–Cl = 2.31 Å, Cu–Cl′ = 2.86 Å, Cu–S = 2.42 Å, Cu–Cu = 3.55 Å, in a distorted square-pyramidal geometry. The compounds were characterized further by EPR and ligand field spectroscopy. Cyclic voltammetry of [Cu(bimtp)Cl₂] and [Cu(bimtp)Cl]₂(ClO₄)₂ yielded quasi-reversible waves with $E°′$ between 0.07 and 0.16 V (with respect to SCE).

Introduction

More than a decade ago the structure of plastocyanin was determined in the reduced as well as the oxidized form.[2,3] The active site of this and other blue copper proteins is constituted from two histidine nitrogens, one methionine thioether sulfur, and one thiolate sulfur of cysteine, surrounding the copper in a distorted tetrahedron. In the last decade the possible synthesis of model compounds has been studied extensively. So far, no compounds mimicking the particular properties of type I copper proteins could be prepared.

Recently a new method has been found, enabling the synthesis of a large variety of 4(5)-substituted imidazole and thioether-containing ligands.[4] In the resulting series of imidazole–thioether ligands, the coordination bite between the imidazole N and the thioether S atom is too small. Coordination compounds containing a five-membered chelate ring are obtained, with the N–metal–S coordination angle never exceeding 84.2°[5-7] A different series

of imidazole–thioether ligands, containing a four-bond N-to-S bridge, was therefore synthesized. The longer N-to-S bridge enables the formation of a six-membered chelate ring, increasing the bite of the ligand. This paper describes the synthesis and characterization of coordination compounds of the ligand 1,5-bis(4-imidazolyl)-3-thiapentane (bimtp) with the transition metal copper and various anions. A schematic drawing of the ligand bimtp is shown in Figure 1. To investigate the binding in detail and to illustrate the chelating nature of the ligand, some X-ray

---

(1) (a) Leiden University. (b) Universita di Siena.
(2) Colman, P. M.; Freeman, H. C.; Guss, J. M.; Mutara, M.; Norris, V. A.; Ranshaw, J. A. M.; Venkatappa, M. P. *Nature* **1978,** *272,* 319.
(3) Freeman, H. C. *Proc. Int. Conf. Coord. Chem., 21st,* **1980,** p 8.
(4) Bouwman, E.; Driessen, W. L. *Synth. Commun.* **1988,** *18,* 1581.
(5) Bouwman, E.; Day, R.; Driessen, W. L.; Tremel, W.; Krebs, B.; Wood, J. S.; Reedijk, J. *Inorg. Chem.* **1988,** *27,* 4614-4618.
(6) Bouwman, E.; de Gelder, R.; de Graaff, R. A. G.; Driessen, W. L.; Reedijk, J. *Recl. Trav. Chim. Pays-Bas* **1988,** *107,* 163-166.
(7) van Steenbergen, A. C.; Bouwman, E.; de Graaff, R. A. G.; Driessen, W. L.; Reedijk, J.; Zanello, P. *J. Chem. Soc., Dalton Trans.,* in press.

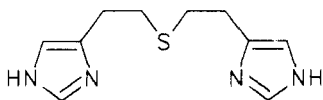*To whom correspondence should be directed.

Figure 1. Schematic drawing of the ligand bimtp.

Table I. Crystallographic Data for [Cu(bimtp)Cl₂] (A), [Cu(bimtp)(NCS)₂] (B), and [Cu(bimtp)Cl]₂(ClO₄)₂ (C)

	A	B	C
chem formula	CuC₁₀H₁₄Cl₂N₄S	CuC₁₂H₁₄N₆S₃	Cu₂C₂₀H₂₈Cl₄N₈O₈
fw	356.8	402.0	841.6
a, Å	7.605 (2)	13.000 (2)	8.703 (2)
b, Å	8.280 (1)	16.400 (3)	13.776 (3)
c, Å	22.644 (5)	8.131 (1)	12.857 (2)
β, deg		105.91 (1)	97.47 (2)
V, Å³	1425.9 (6)	1667 (6)	1528 (3)
Z	4	4	2
T, K	293	293	293
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/c$
ρ_{calcd}, g cm⁻³	1.651	1.59	1.817
μ, cm⁻¹	68.96	53.01	67.39
transm coeff	0.52–1.32	0.62–1.23	0.70–1.15
R^a	0.0319	0.0454	0.0457
$R_w{}^b$	0.0395	0.0473	0.0565

$^a R = \sum(\|F_o\| - |F_c\|)/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]$.

structure determinations have been performed. The redox properties of some of the copper coordination compounds were studied by cyclic voltammetry. A later study will deal with thiolate adducts of these and related Cu(I) complexes.

Experimental Section

Starting Materials. Except for copper(II) thiocyanate, which was prepared in situ (vide infra), all other chemicals were used as commercially available.

Synthesis of 4-Imidazoleethanol Hydrochloride (HisOH) from Histamine Dihydrochloride. A 50-g (0.27-mol) quantity of histamine dihydrochloride was dissolved in 220 mL of acetic acid and 40 mL of water. The solution was cooled until the temperature was below 10 °C. A solution of 27.6 g (0.4 mol) of NaNO₂ in 40 mL of water was added very slowly (during 2 h) to the histamine solution. During the reaction, the temperature was kept below 10 °C with an ice–salt bath. The reaction mixture was stirred at room temperature for 1 h and then heated to 90 °C for 20 min. On cooling, a yellow solution containing a white precipitate resulted. The solvent was removed by evaporation. To the residue (solid and oil) was added water, which, after stirring, was removed again by evaporation. This procedure was repeated once with water, and twice with 2-propanol. Finally, the residue was dissolved in 2-propanol, the mixture was filtered to remove the sodium salts, and the solvent was removed by evaporation. Yield: 57.2 g (100%) of light yellow oil. The ¹H NMR spectrum (solvent (CD₃)₂SO, internal standard HMDS) showed the following signals: 3.0 (t, 2 H, CH₂OH), 3.8 (t, 2 H, im CH₂), 4.2 (broad, NH, OH), 7.0 (s, 1 H, im 5-H), 7.8 ppm (s, 1 H, im 2-H).

Synthesis of 4-(2-Chloroethyl)imidazole (HisCl) from HisOH.[8,9] A 57.2-g (0.27-mol) sample of 4-imidazoleethanol hydrochloride was dissolved in 45 mL of 6 N HCl, and the solvent was removed by evaporation. After an azeotropic distillation with 2-propanol, 25 mL of toluene was added. Then, 100 mL of pure thionyl chloride was added slowly to the mixture. The solution was refluxed for 15 min, whereafter the solvent was distilled off completely. The resulting oil was treated with 2-propanol/ethyl acetate until the product crystallized. Yield: 33.76 g (0.20 mol, 74%) of light yellow, hygroscopic HisCl. Mp: 93–103 °C (lit.[6] 125–126 °C). The ¹H NMR spectrum (solvent (CD₃)₂SO, internal standard HMDS) showed the following signals: 3.1 (t, 2 H, CH₂Cl), 3.5 (broad, NH), 3.9 (t, 2 H, im CH₂), 7.4 (s, 1 H, im 5-H), 9.0 ppm (s, 1 H, im 2-H).

Synthesis of 1,5-Bis(4-imidazolyl)-3-thiapentane (bimtp) from HisCl and Na₂S. A 33.76-g (0.20-mol) quantity 4-(2-chloroethyl)imidazole was dissolved in 100 mL of water, and 8.0 g (0.20 mol) of NaOH in 130 mL of water was added. Then 24.0 g (0.10 mol) of Na₂S·9H₂O was added to this solution. The reaction mixture was refluxed for 6 h, resulting in a yellow solution with an oily deposit. The solution was decanted, and

---

(8) Bloemhoff, W. Ph.D. Thesis, Leiden University, 1974.
(9) Overberger, C. G.; Vorchheimer, N. *J. Am. Chem. Soc.* **1963**, *85*, 951.

Table II

atom	x/a	y/b	z/c	$B(iso)^a$

(a) Atomic Coordinates (Cu(01), Cl(31), Cl(32), and S(05), ×10⁵; Others, ×10⁴) and Equivalent Thermal Parameters (Å²) (C(15), ×10; Others, ×10²) for the Non-Hydrogen Atoms of [Cu(bimtp)Cl₂] (A)

atom	x/a	y/b	z/c	$B(iso)^a$
Cu(01)	64880 (13)	47675 (12)	88690 (4)	252 (2)
Cl(31)	79382 (13)	72988 (12)	85492 (4)	338 (3)
Cl(32)	34382 (13)	48745 (12)	88874 (4)	388 (3)
C(03)	9717 (7)	3281 (7)	8024 (2)	361 (14)
C(04)	9829 (7)	2023 (7)	8500 (2)	389 (14)
S(05)	83342 (13)	23698 (12)	91268 (4)	285 (3)
C(06)	9788 (7)	2961 (6)	9718 (2)	310 (13)
C(07)	9829 (7)	4779 (6)	9843 (2)	305 (12)
N(11)	5624 (7)	3041 (6)	7194 (2)	402 (14)
C(12)	5125 (8)	3710 (7)	7706 (2)	366 (14)
N(13)	6486 (5)	3920 (5)	8056 (1)	284 (10)
C(14)	7939 (7)	3332 (7)	7756 (2)	295 (12)
C(15)	7414 (8)	2806 (7)	7219 (2)	39 (2)
N(21)	5916 (7)	6285 (5)	10582 (2)	319 (11)
C(22)	5343 (8)	5983 (6)	10040 (2)	298 (13)
N(23)	6635 (5)	5422 (5)	9705 (1)	238 (9)
C(24)	8123 (7)	5376 (6)	10060 (2)	250 (11)
C(25)	7687 (8)	5910 (6)	10602 (2)	333 (14)

(b) Atomic Coordinates (Cu(01) and S(05), ×10⁵; Others, ×10⁴) and Equivalent Thermal Parameters (Å²) (Cu(01), S(05), S(83), and S(93), ×10²; Others, ×10) for the Non-Hydrogen Atoms of [Cu(bimtp)(NCS)₂] (B)

atom	x/a	y/b	z/c	$B(iso)^a$
Cu(01)	67367 (8)	13873 (6)	81952 (12)	363 (2)
C(03)	6626 (5)	2953 (4)	10774 (7)	50 (2)
C(04)	7098 (5)	3428 (4)	9596 (7)	57 (2)
S(05)	71643 (8)	28976 (6)	76646 (25)	426 (4)
C(06)	5991 (5)	3262 (4)	6034 (7)	46 (2)
C(07)	5079 (5)	2666 (4)	5528 (7)	44 (2)
N(11)	8419 (4)	1379 (3)	13257 (6)	41 (1)
C(12)	8125 (4)	1081 (4)	11673 (7)	38 (2)
N(13)	7450 (3)	1577 (2)	10620 (5)	33 (1)
C(14)	7311 (5)	2236 (4)	11578 (7)	37 (2)
C(15)	7096 (5)	2128 (4)	13217 (7)	45 (2)
N(21)	5529 (5)	906 (4)	3079 (7)	60 (2)
C(22)	6153 (5)	743 (4)	4652 (9)	51 (2)
N(23)	6060 (4)	1329 (3)	5706 (6)	41 (1)
C(24)	5354 (5)	1900 (4)	4758 (7)	41 (2)
C(25)	5020 (5)	1627 (4)	3149 (9)	55 (2)
N(81)	5304 (4)	1285 (3)	8652 (6)	48 (2)
C(82)	4523 (5)	1017 (3)	8804 (6)	33 (2)
S(83)	3434 (2)	639 (1)	9078 (2)	534 (5)
N(91)	7957 (4)	706 (3)	7950 (6)	46 (2)
C(92)	8726 (5)	605 (3)	7528 (7)	35 (2)
S(93)	9787 (2)	451 (1)	6893 (2)	475 (5)

(c) Atomic Coordinates (Cu(01), Cl(02), S(05), and Cl(80), ×10⁵; Others, ×10⁴) and Equivalent Thermal Parameters (Å²) (Cu(01), ×10³; O(82) and O(84), ×10; Others, ×10²) for the Non-Hydrogen Atoms of [Cu(bimtp)Cl]₂(ClO₄)₂ (C)

atom	x/a	y/b	z/c	$B(iso)^a$
Cu(01)	8148 (5)	38166 (4)	51033 (3)	3082 (14)
Cl(02)	−17432 (8)	42216 (7)	51965 (6)	391 (2)
C(03)	3140 (4)	3885 (3)	3260 (3)	392 (9)
C(04)	3944 (4)	3090 (3)	3917 (3)	419 (9)
S(05)	30317 (9)	27675 (7)	50645 (6)	361 (2)
C(06)	4510 (4)	3128 (3)	6130 (3)	442 (10)
C(07)	4286 (4)	4126 (3)	6545 (3)	406 (9)
N(11)	−758 (4)	3364 (2)	2009 (2)	423 (8)
C(12)	−936 (4)	3407 (3)	3025 (3)	382 (8)
N(13)	406 (3)	3603 (2)	3593 (2)	327 (6)
C(14)	1493 (4)	3667 (3)	2893 (3)	340 (7)
C(15)	751 (5)	3530 (3)	1918 (3)	413 (9)
N(21)	1298 (4)	4283 (3)	8262 (2)	447 (8)
C(22)	479 (4)	4069 (3)	7343 (3)	378 (8)
N(23)	1407 (3)	4008 (2)	6604 (2)	315 (6)
C(24)	2894 (4)	4196 (2)	7101 (2)	343 (7)
C(25)	2821 (5)	4367 (3)	8124 (3)	436 (9)
Cl(80)	73961 (10)	10272 (7)	43858 (16)	441 (2)
O(81)	6721 (4)	1500 (3)	5191 (2)	628 (9)
O(82)	8984 (4)	985 (5)	4686 (3)	133 (3)
O(83)	7063 (4)	1493 (3)	3415 (2)	723 (11)
O(84)	6780 (7)	76 (3)	4277 (4)	113 (2)

$^a B_{eq} = (8/3) \pi^2 \text{ trace } U$.

Table III. Selected Bond Lengths (Å), Bond Angles (deg), and Hydrogen-Bond Lengths (Å)

(a) [Cu(bimtp)Cl₂] (A)[a]			
Cu(01)–Cl(31)	2.477 (1)	Cu(01)–N(13)	1.970 (4)
Cu(01)–Cl(32)	2.321 (1)	Cu(01)–N(23)	1.972 (3)
Cu(01)–S(05)	2.501 (1)		
Cl(31)–Cu(01)–Cl(32)	114.70 (5)	Cl(32)–Cu(01)–N(13)	91.7 (1)
Cl(31)–Cu(01)–S(05)	119.35 (5)	Cl(32)–Cu(01)–N(23)	91.7 (1)
Cl(31)–Cu(01)–N(13)	91.6 (1)	S(05)–Cu(01)–N(13)	86.3 (1)
Cl(31)–Cu(01)–N(23)	91.3 (1)	S(05)–Cu(01)–N(23)	87.8 (1)
Cl(32)–Cu(01)–S(05)	125.95 (6)	N(13)–Cu(01)–N(23)	174.1 (2)
Cl(31)–N(21)′	3.221 (4)	Cl(31)–N(11)″	3.248 (5)
Cl(31)–H(21)′	2.282 (4)	Cl(31)–H(11)″	2.244 (5)

(b) [Cu(bimtp)(NCS)₂] (B)[b]			
Cu(01)–S(05)	2.600 (2)	Cu(01)–N(81)	2.004 (5)
Cu(01)–N(13)	1.960 (4)	Cu(01)–N(91)	1.994 (5)
Cu(01)–N(23)	1.976 (4)		
S(05)–Cu(01)–N(13)	87.2 (1)	N(13)–Cu(01)–N(81)	92.0 (2)
S(05)–Cu(01)–N(23)	86.1 (1)	N(13)–Cu(01)–N(91)	91.1 (2)
S(05)–Cu(01)–N(81)	111.2 (5)	N(23)–Cu(01)–N(81)	90.6 (2)
S(05)–Cu(01)–N(91)	107.8 (2)	N(23)–Cu(01)–N(91)	90.8 (2)
N(13)–Cu(01)–N(23)	173.3 (2)	N(81)–Cu(01)–N(91)	141.0 (2)
S(93)–H(11)′	2.325 (5)	S(83)–H(21)″	2.522 (6)
S(93)–N(11)′	3.367 (5)	S(83)–N(21)″	3.552 (6)

(c) [Cu(bimtp)Cl]₂(ClO₄)₂ (C)[c]			
Cu(01)–Cu(01)*	3.5518 (9)	Cu(01)–N(13)	1.950 (3)
Cl(02)–Cl(02)*	3.803 (2)	Cu(01)–N(23)	1.948 (3)
Cu(01)–Cl(02)	2.3132 (8)	Cu(01)–Cl(02)*	2.861 (1)
Cu(01)–S(05)	2.4162 (9)		
Cl(02)–Cu(01)–S(05)	157.18 (4)	S(05)–Cu(01)–Cl(02)*	108.78 (3)
Cl(02)–Cu(01)–N(13)	92.05 (8)	N(13)–Cu(01)–N(23)	175.2 (1)
Cl(02)–Cu(01)–N(23)	92.78 (8)	N(13)–Cu(01)–Cl(02)*	91.53 (8)
Cl(02)–Cu(01)–Cl(02)*	93.99 (3)	N(23)–Cu(01)–Cl(02)*	87.85 (8)
S(05)–Cu(01)–N(13)	86.09 (8)	Cu(01)–Cl(02)–Cu(01)*	86.01 (3)
S(05)–Cu(01)–N(23)	89.56 (8)		
O(81)–H(11)′	2.12 (5)	O(81)–N(11)′	2.996 (4)
O(82)–H(21)″	2.23 (5)	O(82)–N(21)″	2.916 (5)
O(82)–H(21)‴	2.93 (5)	O(82)–N(21)‴	3.562 (6)

[a] Symmetry positions: (′) $x + 0.5, -y + 1.5, -z + 2$; (″) $-x + 1, 0.5 + y, -z + 1.5$. [b] Symmetry positions: (′) $x, y, 1 - z$; (″) $1 - x, -y, 1 - z$. [c] Symmetry positions: (*) $-x, 1 - y, 1 - z$; (′) $1 + x, 0.50 - y, 0.50 + z$; (″) $1 + x, 0.50 - y, -0.50 + z$; (‴) $1 - x, 0.50 + y, 1.50 - z$.

Figure 2. ORTEP projection and atomic labeling of [Cu(bimtp)Cl₂] (A). For clarity the hydrogen atoms are omitted.

Figure 3. ORTEP projection and atomic labeling of [Cu(bimtp)(NCS)₂] (B). For clarity the hydrogen atoms are omitted.

the solvent was removed by evaporation. This product, a mixture of bimtp and salts, was recrystallized from water. The oily product was treated with ethanol, and sodium salts were removed by filtration. Most of the product crystallized from the oil on treatment with water. The remaining oil solidified after several weeks. Yield: 16.2 g (0.073 mol, 73%) of almost white bimtp. Mp: 132–136 °C. Anal. Found (calcd) for C₁₀H₁₄N₄S: C, 54.1 (54.1); H, 6.5 (6.3); N, 25.3 (25.2); S, 14.6 (14.4). The ¹H NMR spectrum (solvent (CD₃)₂SO, internal standard SiMe₄) showed the following signals: 2.7 (s, 4 H, CH₂CH₂), 3.4 (broad, NH), 6.7 (s, 1 H, im 5-H), 7.4 ppm (s, 1 H, im 2-H).

Synthesis of the Copper Compounds. The coordination compounds were prepared by dissolving the appropriate (hydrated) metal salt (2 mmol) in 10 mL of warm ethanol and adding this solution to a solution of the ligand bimtp (2 mmol) in 40 mL of boiling ethanol. After filtration of the hot reaction mixture, the complex crystallized on cooling. For the preparation of the thiocyanate compound, a solution of copper nitrate (2 mmol) in 10 mL of ethanol was added to the solution of the ligand (2 mmol) and ammonium thiocyanate (NH₄NCS, 4 mmol) in 40 mL of ethanol.

N.B. *Warning!* One of the compounds described here contains perchlorate anions. Although no accidents with perchlorates occurred during the experimental work described in this paper, the use of perchlorates is hazardous because of the possibility of explosion, especially when the compounds are dry.

Analysis. Metal analyses were carried out complexometrically with Na₂H₂edta as the complexing agent.[10] Halogen analyses were performed by potentiometric titrations with silver nitrate.[10] C, H, and N analyses were performed by the microanalytical laboratory of University College, Dublin.

Spectroscopic Measurements. Infrared spectra in the 4000–200-cm⁻¹ range of the samples, pelleted in KBr, were recorded on a Perkin-Elmer 580 spectrophotometer. Ligand field spectra of the solids (300–2000 nm)
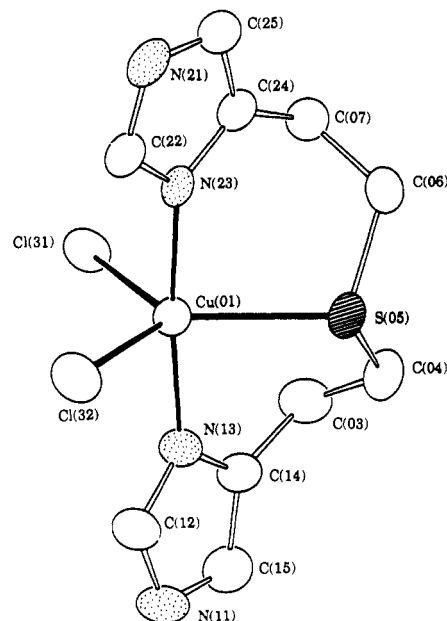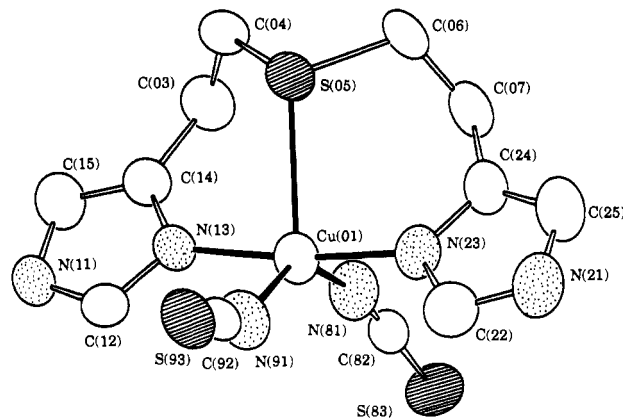
and of the solutions in DMSO with supporting electrolytes (450–1600 nm) were taken on a Perkin-Elmer 330 spectrophotometer equipped with a data station. Electron paramagnetic resonance (EPR) spectra of the powdered copper(II) compounds and of the frozen solutions in DMSO were obtained by using a Varian E-3 spectrometer at X-band frequencies. NMR spectra were recorded on a JNM-FX 200 spectrometer.

Electrochemical Measurements. Cyclic voltammetry was performed in a three-electrode cell, consisting of a platinum working electrode, surrounded by a platinum spiral counter electrode, and an aqueous saturated calomel reference electrode (SCE) mounted with a Luggin capillary. All cyclic voltammetry experiments were carried out at room temperature. A BAS 100A electrochemical analyzer was used as the polarizing unit. Controlled-potential coulometric tests were performed in a H-shaped cell with anodic and cathodic compartments separated by a sintered-glass disk. The working macroelectrode was a platinum gauze; a mercury pool was used as the counter electrode. An Amel Model 551 potentiostat with an associated coulometer (Amel Model 558 integrator) was employed. Under the ambient experimental conditions the ferrocenium–ferrocene couple was located at +0.40 V.

Data Collection and Structure Refinement. The reflection intensities of [Cu(bimtp)Cl₂] (A), [Cu(bimtp)(NCS)₂] (B), and [Cu(bimtp)Cl]₂-(ClO₄)₂ (C) were measured and collected on a four-circle Enraf-Nonius CAD-4 diffractometer with monochromatized Cu Kα radiation (λ = 1.541 78 Å). For all three structures crystal data and additional particulars of the data collection and refinement are presented in Table I. The calculations were performed on the Leiden University Amdahl 5860 computer. Intensities were corrected for Lorentz and polarization effects. The position of the heavy metal in A–C was obtained from Patterson maps. The other non-hydrogen atoms of A–C were located by using the program AUTOFOUR.[11] Absorption correction was applied in all cases.

(10) Vogel, A. I. *Quantitative Inorganic Analyses*; Longmans: London, 1961.

(11) Kinneging, A. J.; de Graaff, R. A. G. *J. Appl. Crystallogr.* **1984,** *17,* 364.
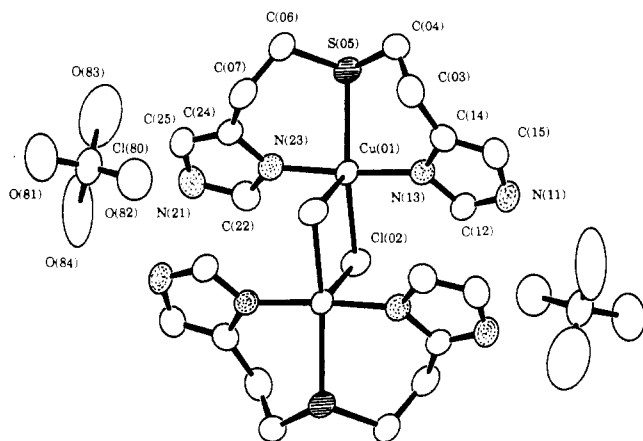
Figure 4. ORTEP projection and atomic labeling of [Cu(bimtp)Cl]$_2$-(ClO$_4$)$_2$ (C). For clarity the hydrogen atoms are omitted.

Transmission factors were calculated on the basis of models of the crystal by using a method given by de Graaff[12] (B, C) or estimated by using the program DIFABS[13] (A). The structures were refined by full-matrix least squares. Refinement was continued until all shifts were smaller than one-third of the parameters involved. Scattering factors were taken from ref 14. Hydrogen atoms were located from difference Fourier maps. The non-hydrogen atoms were refined anisotropically. The positional and isotropic thermal parameters of the hydrogen atoms of C were refined. The function minimized was $\sum w(||F_o| - |F_c||)^2$ with $w = 1/\sigma^2(F)$. The positional parameters of the hydrogen atoms of A and B were not refined independently. One overall B_{eq} value was refined (ultimate values of 5.1 Å^2 (A) and 7.9 Å^2 (B)).

The fractional coordinates of the non-hydrogen atoms of A–C are listed in Table II. Selected bond distances, bond angles, and hydrogen-bonding distances are given in Table III. The estimated standard deviations in the distances and angles were calculated from the full correlation matrix. Lists of the atomic coordinates of the hydrogen atoms, of the non-hydrogen anisotropic thermal parameters, of the bond distances and angles, and of the observed and calculated structure factors are available.[15]

Results and Discussion

[Cu(bimtp)Cl$_2$] (A). An ORTEP[16] drawing of [Cu(bimtp)Cl$_2$], also showing the atomic numbering scheme, is depicted in Figure 2. The compound (1,5-bis(4-imidazolyl)-3-thiapentane)dichlorocopper(II) forms the asymmetric unit in this orthorhombic space group ($P2_12_12_1$). Addison et al. have proposed a structural index τ for these geometries,[17] which has been defined as $\tau = (\beta - \alpha)/60$, with α and b being the two largest coordination angles. In a perfect square-pyramidal geometry, τ equals 0, while it equals 1 in a perfect trigonal-bipyramidal geometry. For [Cu(bimtp)Cl$_2$], τ equals 0.99; hence copper(II) is coordinated by an almost ideal trigonal bipyramid. Both imidazole nitrogens are in the axial positions (Cu–N = 1.97 Å). The thioether sulfur and both chloride anions constitute the equatorial plane (Cu–S = 2.50, Cu–Cl = 2.48 and 2.33 Å). The N–Cu–S angles are larger than those found in compounds containing three-atom N-to-S bridges. The angles between N(13)–Cu–S and N(23)–Cu–S are 86.1 and 88.4°, respectively, compared to, for instance, 82.0 and 83.0° in the case of 1,6-bis(4-imidazolyl)-2,5-dithiahexane[5] and 1,6-bis(5-methyl-4-imidazolyl)-2,5-dithiahexane.[5] The imidazole rings are planar, with deviations from the least-squares plane less than 0.008 Å. Hydrogen bonding occurs between the Cl$^-$ ions and the imidazole NH; relevant distances are given in Table IIIa.

[Cu(bimtp)(NCS)$_2$] (B). An ORTEP[16] projection of the compound [Cu(bimtp)(NCS)$_2$], also showing the atomic numbering,

is depicted in Figure 3. The compound crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the cell. The asymmetric unit consists of one molecule of (1,5-bis-(4-imidazolyl)-3-thiapentane)bis(thiocyanato-N)copper(II). For [Cu(bimtp)(NCS)$_2$], the structural index τ^{17} equals 0.76; hence the copper(II) ion is in a distorted trigonal-bipyramidal geometry. The geometry is distorted in the direction of a square-based pyramid. Both imidazole nitrogens and both thiocyanate nitrogens form the square plane. If, for the description of the structure, the geometry is considered to be a trigonal bipyramid, then the two imidazole nitrogens are in the axial positions (Cu–N(13) = 1.95, Cu–N(23) = 1.98 Å) and both thiocyanate nitrogens and the thioether sulfur are in the trigonal plane. The distortion from trigonal bipyramidal is caused by the thiocyanates (N(41)–Cu–N(31) = 140.9, N(41)–Cu–S = 111.0, N(31)–Cu–S = 108.0°; Cu–N(31) = 1.998, Cu–N(41) = 1.990, Cu–S = 2.597 Å). The thiocyanates are not coordinated linearly: the bond angle Cu–N(81)–C(82) equals 161.8° and Cu–N(91)–C(92) equals 152.6°. This deviation from 180° is rather common.[18] The smallest observed Cu–NCS bond angle known[19] is 128.6°. The imidazole N to copper to sulfur bond angles are 86.1 and 87.2°, only slightly larger than for Cu(sbi)(NO$_3$)$_2$[7] (83.9 and 84.2°) (sbi = bis((5-methyl-4-imidazolyl)methyl) sulfide). The imidazole rings are planar, with deviations from the least-squares plane less than 0.005 Å. Hydrogen bridges occur between the imidazole NH and the thiocyanate sulfur atom; relevant distances are given in Table IIIb.

[Cu(bimtp)Cl]$_2$(ClO$_4$)$_2$ (C). An ORTEP[16] projection of the structure of [Cu(bimtp)Cl]$_2$(ClO$_4$)$_2$ is shown in Figure 4. The compound crystallizes in the monoclinic space group $P2_1/c$ with two dinuclear cations in the cell. The asymmetric unit consists of half of a molecule of bis[(μ-chloro)(1,5-bis(4-imidazolyl)-3-thiapentane)copper(II)] bis(perchlorate). For [Cu(bimtp)Cl]$_2$-(ClO$_4$)$_2$, the structural index τ^{17} equals 0.46. In agreement with this τ value, the copper(II) ion, surrounded by the tridentate ligand bimtp and two chloride anions, is in a distorted square-pyramidal geometry (N–Cu–N = 175.2, N–Cu–S = 86.1 and 89.6°, S–Cu–Cl = 157.2, S–Cu–Cl' = 108.8°). The perchlorate ions do not participate in the coordination. The imidazole rings are planar, with deviations from the least-squares planes less than 0.003 Å. The copper to sulfur bond distance is significantly smaller (2.416 Å) than in compounds A and B (Cu–S: 2.50 (A), 2.597 Å (B)). The Cu–Cu' dimer distance is 3.552 Å. Compared to Cu–Cu distances in dichloro-bridged compounds described in the literature, this value is a normal one (Cu–Cu' = 3.418 Å,[20] 3.575 Å,[21] 3.416–3.749 Å[22]). The Cu–Cl distance is 2.313 Å and Cu–Cl' equals 2.861 Å, where Cl' occupies the apical position. The imidazole rings are planar, with deviations from the least-squares planes less than 0.008 (2) Å. The perchlorate anions are hydrogen-bonded to the imidazole NH's, forming chains of dimers. Hydrogen-bonding distances are given in Table IIIc.

Spectroscopic Results for Cu(II) Compounds Containing bimtp. Ligand field, EPR, infrared, and X-ray data for the copper compounds with bimtp are given in Table IV. The characteristic infrared vibrations of the anions NCS$^-$ (2100 cm^{-1}), NO$_3^-$ (1300 cm^{-1}), ClO$_4^-$ (1100 cm^{-1}), and BF$_4^-$ (1050 cm^{-1}) were easily recognized. The infrared spectra, as well as the metal and halogen contents analyzed, indicate the correctness of the stoichiometry proposed. The ligand field spectrum of [Cu(bimtp)Cl$_2$] (A) already suggested a trigonal-bipyramidal geometry for the copper ion, which is confirmed by the structure determination. [Cu(bimtp)Cl$_2$] and [Cu(bimtp)Br$_2$] have identical infrared spectra and very similar ligand field spectra, and the inverted axial EPR spectra of both compounds have the same g values. However, X-ray powder photographs show that [Cu(bimtp)Cl$_2$] and [Cu(bimtp)Br$_2$] are not isomorphous.

(12) de Graaff, R. A. G. *Acta Crystallogr., Sect. A* **1973**, *29*, 298.
(13) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158–166.
(14) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.
(15) Supplementary material.
(16) Johnson, C. K. ORTEP. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.
(17) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

(18) Norbury, A. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 231.
(19) Korvenranta, J.; Pajunen, A. *Suom. Kemistil. B* **1970**, *43*, 119.
(20) Kwiatkowski, E.; Kwiatkowski, M.; Mrozinski, J.; Ho, D. M.; Deutsch, E. *Inorg. Chim. Acta* **1989**, *158*, 37–42.
(21) Drake, R. F.; Crawford, V. H.; Laney, N. W.; Hatfield, W. E. *Inorg. Chem.* **1974**, *13*, 1246.
(22) Marsh, W. E.; Patel, K. C.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1983**, *22*, 511–515.

Table IV. Infrared, X-ray, Ligand Field, and EPR Spectroscopic Data for the Copper(II) Compounds

compd	IR[a]	X-ray[a,b]	LF bands[c]	EPR[d]
[Cu(bimtp)(NCS)$_2$]	A	I	12.4 (br), 27.4	$g_1 = 2.26, g_2 = 2.15, g_3 = 2.04$
[Cu(bimtp)Br$_2$]	B	II	13.0 (br), 28.4	$g_\perp = 2.19, g_\parallel = 2.05$
[Cu(bimtp)Cl$_2$]	B'	III	12.1 (br), 29.2	$g_\perp = 2.19, g_\parallel = 2.05$
[Cu(bimtp)(NO$_3$)$_2$]	C	IV	29.8, 16.3, 11.8 (br)	$g_1 = 2.22, g_2 = 2.12, g_3 = 2.08$
[Cu(bimtp)Cl]$_2$(ClO$_4$)$_2$	D	V	15.4	$g_1 = 2.19, g_2 = 2.14, g_3 = 2.05$
[Cu(bimtp)Cl]$_2$(BF$_2$)$_2$·2H$_2$O	E	V'	13.6	$g_1 = 2.16, g_2 = 2.09, g_3 = 2.01$

[a] The same capital or Roman numeral primed when identical or very similar. [b] Guinier photographs of crystalline material ("powder patterns"). [c] d–d transitions in 10^3 cm^{-1}. [d] Solids at room temperature.
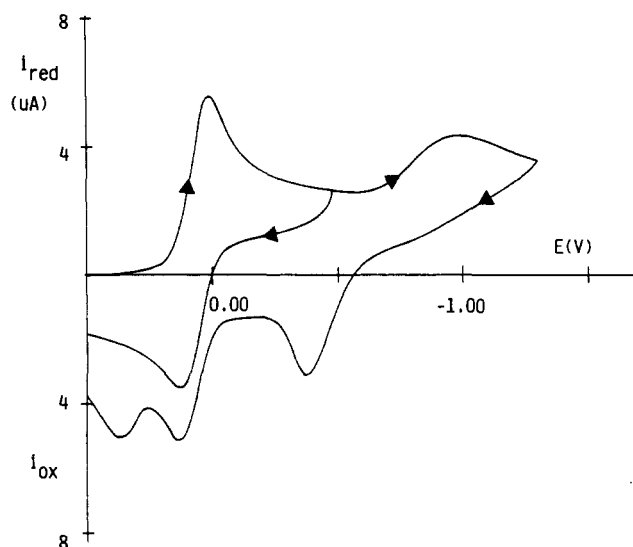
Figure 5. Cyclic voltammogram recorded at a platinum electrode on a deaerated DMSO solution containing [Cu(bimtp)Cl$_2$] (1.7×10^{-3} mol dm^{-3}) and (NEt$_4$)(ClO$_4$) (0.1 mol dm^{-3}). Scan rate = 0.2 V s^{-1}.

From the crystal structure of [Cu(bimtp)(NCS)$_2$] it is known that the copper(II) ion has a tetragonally distorted trigonal-bipyramidal geometry. The EPR spectrum is rhombic. The ligand field spectrum of [Cu(bimtp)(NCS)$_2$] is intermediate between a trigonal-bipyramidal geometry and a tetragonal-pyramidal geometry around the Cu(II) ion.

The compound [Cu(bimtp)(NO$_3$)$_2$] has a different infrared spectrum, compared to the other compounds. The ligand field spectrum of [Cu(bimtp)(NO$_3$)$_2$] suggests a square-based-pyramidal geometry for the copper(II) ion, whereas the EPR spectrum appears to be rhombic. Probably, [Cu(bimtp)(NO$_3$)$_2$] has a distorted square-based-pyramidal geometry.

The ligand field spectrum of [Cu(bimtp)Cl]$_2$(ClO$_4$)$_2$ (C) already suggests a square-planar or square-pyramidal geometry for the copper(II) ion. This is in agreement with the crystal structure. The EPR spectrum of [Cu(bimtp)Cl]$_2$(ClO$_4$)$_2$ appears as rhombic. The crystal shows that this compound has a dinuclear structure, but the complicated EPR spectrum of the frozen solution shows only very weak dimeric signals at 2590–2695 G with A = 50 G and no half-field signal for scanning in the range 700–5700 G. The infrared spectrum of [Cu(bimtp)Cl]$_2$(BF$_2$)$_2$·2H$_2$O is different from the infrared spectrum of [Cu(bimtp)Cl]$_2$(ClO$_4$)$_2$. The ligand field spectra and the EPR spectra of both compounds look similar but not identical. X-ray powder patterns show that [Cu(bimtp)Cl]$_2$(ClO$_4$)$_2$ and [Cu(bimtp)Cl]$_2$(BF$_4$)$_2$·2H$_2$O are almost isomorphous. [Cu(bimtp)Cl]$_2$(BF$_4$)$_2$·2H$_2$O is therefore expected to have the same geometry as [Cu(bimtp)Cl]$_2$(ClO$_4$)$_2$, with water molecules in noncoordinating lattice positions.

Electrochemistry. Mononuclear Complexes. Figure 5 shows the cyclic voltammetric response exhibited by [Cu(bimtp)Cl$_2$] in a dimethyl sulfoxide solution. Two consecutive steps of reduction are visible; only the first shows indications of chemical reversibility.

Controlled-potential coulometry (E_w = −0.2 V) indicates the first reduction to involve the addition of one electron per molecule. Analyzing[23] the cyclic voltammograms relevant to a Cu(II)/Cu(I)

Table V. Relevant Electrochemical Parameters for the Two Successive One-Electron Reductions of the Mononuclear Compounds in Dimethyl Sulfoxide Solution

compd	$E^{\circ\prime}$(Cu(II)/Cu(I)), V	ΔE_p,[a] mV	E_p(Cu(I)/Cu(0)), V
[Cu(bimtp)Cl$_2$]	+0.07	130	−0.94
[Cu(bimtp)Br$_2$]	+0.13	105	−1.21
[Cu(bimtp)(NCS)$_2$]	+0.13	132	−0.75
[Cu(bimtp)(NO$_3$)$_2$]	+0.16	139	−0.90

[a] Measured at 0.2 V s^{-1}, at which the ΔE_p value for the ferrocenium/ferrocene couple was 63 mV.

redox reaction, with a scan rate v varying from 0.02 to 5.12 V s^{-1}, shows that (i) the peak current ratio i_{pa}/i_{pc} is constant and equal to 1, (ii) the current function $i_{pc}v^{-1/2}$ is substantially constant, (iii) the difference in peak potential values ΔE_p ($= E_{pa} - E_{pc}$) progressively increases from 92 to 312 mV. These findings clearly indicate a simple one-electron mechanism for the reduction, quasi-reversible in character. On completion of the first reduction step, a colorless solution is obtained. The cyclic voltammogram obtained from this solution is almost identical with the one shown in Figure 5, illustrating the chemical reversibility of the first redox step. A minor complication, an extra peak at $E^{\circ\prime}$ = +0.30 V (in a peak:current ratio of about 1:4 with respect to the [Cu(bimtp)Cl$_2$]$^{-/0}$ system), is probably caused by a slow chemical reaction of the end product of the first reduction step. A further illustration of the reversibility of the first step is the complete regeneration of the starting material on oxidizing of the colorless solution (E_w = +0.15 V).

The second step, cathodic reduction to Cu(0), completely destroys the molecular structure. This reaction was not investigated further.

Qualitatively similar results are obtained for all the copper(II) complexes presented here; the most relevant electrochemical parameters are summarized in Table V. The peak-to-peak separation ΔE_p for the Cu(II)/Cu(I) electron transfers is of some relevance for the stereochemical reorganizations accompanying this redox change.[24] Electrochemically reversible one-electron transfer (ΔE_p = 60 mV) precludes significant structural rearrangement, while quasi-reversibility usually indicates that some geometrical changes are taking place without changing the actual framework of the structure.[25]

Dinuclear Complexes. Figure 6 illustrates the redox pattern exhibited by [Cu(bimtp)Cl]$_2$(ClO$_4$)$_2$ in a dimethyl sulfoxide solution. In the dinuclear complexes the reduction proceeds in two steps as well. From Figure 6b, the first reduction seems to involve two nearly overlapping electron transfers. Controlled-potential coulometric tests (E_w = −0.2 V) confirm the consumption of two electrons per molecule. The resulting colorless solution gives rise to a cyclic voltammogram reversed with respect to the one shown in Figure 6b. Also in this case, a very minor spurious peak system, located at $E^{\circ\prime}$ = +0.30 V, arises, but the amount of the relevant byproduct is even smaller than that found in the related mononuclear complex. Once again, exhaustive reoxidation at +0.3 V completely regenerates the initial green copper(II) dimer solution.

(23) Brown, E. R.; Sandifer, J. R. *Physical Methods of Chemistry. Electrochemical Methods*; Rossiter, B. W., Hamilton, J. F., Eds.; Wiley: New York, 1986; Vol. 2, Chapter 4.

(24) Zanello, P. *Comments Inorg. Chem.* **1988**, 8, 45.
(25) Zanello, P. *Electrochemistry of Mononuclear Copper Complexes. Structural Reorganizations Accompanying Redox Changes in Stereochemistry of Organometallic and Inorganic Compounds*; Bernal, I., Ed.; Elsevier: Amsterdam, in press; Vol. IV.

E (VOLT)
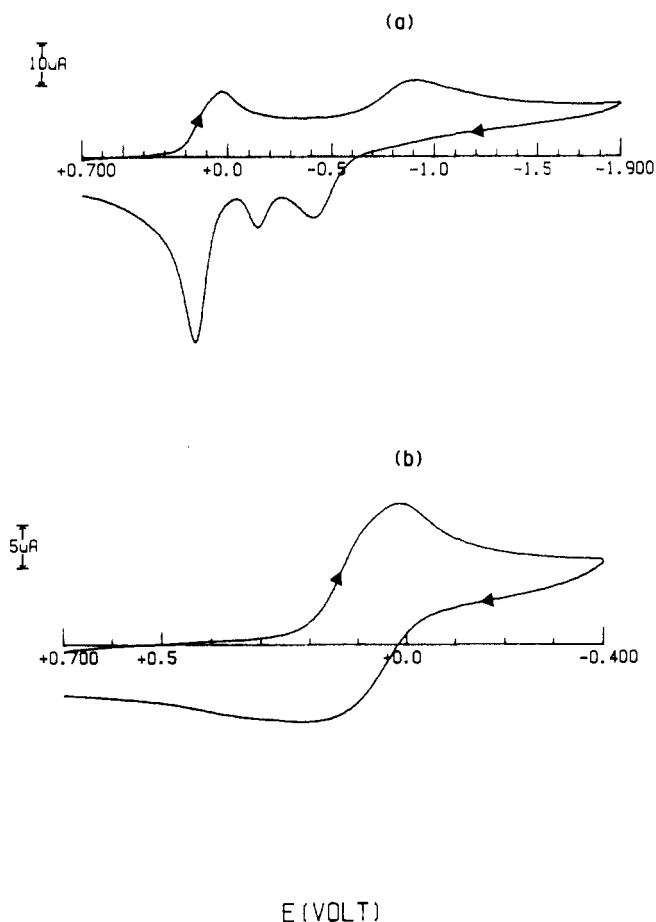
Figure 6. Cyclic voltammograms recorded at a platinum electrode on a deaerated DMSO solution containing $[Cu(bimtp)Cl]_2(ClO_4)_2$ (1.37 × 10^{-3} mol dm^{-3}) and $(NEt_4)(ClO_4)$ (0.1 mol dm^{-3}). Scan rate = 0.2 V s^{-1}. Scan ranges: (a) between +0.7 and −1.9 V; (b) between +0.7 and −0.4 V.

The redox reaction $Cu^{II}Cu^{II}/Cu^{I}Cu^{I}$ is clearly almost perfectly reversible. The two electrons enter the dimer at potentials that are nearly equal ($E^{o\prime}$ = +0.09 V). This can be interpreted as

the successive addition of one electron to two separate, electrostatically noninteracting centers, for which a difference in potential values of 36 mV is theoretically foreseen.[26] These data agree with the nonbonding Cu···Cu distance in the dimer (3.55 Å). Finally, as shown in Figure 6a, the dicopper complex undergoes a further reduction step at E_p = −0.88 V, most likely attributable to the single-stepped two-electron reduction $Cu^{I}Cu^{I}/Cu^{0}Cu^{0}$, which leads to rapid destruction of the complex.

No significant difference in redox pattern has been displayed by $[Cu(bimtp)Cl]_2(BF_4)_2\cdot 2H_2O$, thus confirming the spectral evidence of a peripheral coordination of water molecules.

Concluding Remarks

The attempts to synthesize a new imidazole thioether ligand have been successful. Coordination compounds containing a six-membered chelate ring are formed. As expected, the coordination angle between the imidazole N and the thioether S atom appeared to be larger than in five-membered chelate rings; the imidazole nitrogen–copper–thioether sulfur bond angles described in this article are between 86.1 and 89.6°, compared to 83.9 and 84.2° in $Cu(sbi)(NO_3)_2$.[7] The redox potentials of the copper complexes with the ligand bimtp are quite high (between +0.07 and +0.16 V vs. SCE). The copper(II)/copper(I) reduction appears to be chemically reversible. The rather high redox potential indicates that copper(I) is stabilized by the ligand bimtp.

(26) Gagné, R. R.; Koval, C. A.; Smith, T. J.; Cimolino, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4571.