The Influence of Co-ordination Number on Copper(I)–(II) Redox Interconversions. Part 1. Reduction of Five-co-ordinate (±)-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradecanecopper(II) Complexes, $[Cu^{II}(tet\text{-}b)X]^+$ (X^- = Cl^-, Br^-, or Thiourea), with Cr^{2+}, V^{2+}, and $[Ru(NH_3)_6]^{2+}$ †

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The 1 : 1 Cr^{2+} reductions of the five-co-ordinate $[Cu^{II}(tet\text{-}b)X]^+$ complexes (X^- = Cl^-, Br^-, and thiourea) have been studied. At 25 °C, I = 0.20M (lithium *p*-toluenesulphonate), reactions are independent of $[H^+]$ (0.01—0.20M) and rate constants (l mol^{-1} s^{-1}) are 17.9 (Cl^-), 21.4 (Br^-), and 81 (thiourea). The Cr^{III} products are $[CrCl]^{2+}$, $[CrBr]^{2+}$, and *S*-bonded $[Cr(thiourea)]^{3+}$. With V^{2+} as reductant rate constants (l mol^{-1} s^{-1}, 25 °C) and activation parameters $\Delta H^\ddagger$ (kcal mol^{-1}) and $\Delta S^\ddagger$ (cal K^{-1} mol^{-1}) are 0.055, 9.9, and −31.0 (Cl^-) and 0.020, 12, and −27 (thiourea), respectively. Less extensive studies with X^- = Br^- give a rate constant at 50 °C of *ca.* 0.03 l mol^{-1} s^{-1}. Slow $[Ru(NH_3)_6]^{2+}$ reduction of $[Cu^{II}(tet\text{-}b)Cl]^+$, $k \leqslant 10^{-3}$ l mol^{-1} s^{-1} at 20 °C rules out an outer-sphere process for the corresponding V^{2+} reduction and, since, the parameters obtained are not in the substitution-controlled range, suggests an inner-sphere electron-transfer-controlled process. The extreme reluctance of $[Cu^{II}(tet\text{-}b)X]^+$ complexes to react by an outer-sphere process is noted.

STUDIES on redox reactions involving the copper(I) and copper(II) aquo-ions have indicated a strong preference for inner-sphere processes.[1-8] This tendency, like that for Cr^{2+} reactions, can be ascribed to the high ligand-reorganization energy requirement for processes involving tetragonally distorted octahedral ions, in this case copper(II).

Recent studies on the reactions of copper-containing proteins have shown that reactions of the outer-sphere type can occur, and in many cases are extremely rapid.[9] Although detailed crystal structures are not yet known considerable evidence has been obtained to indicate that the blue proteins have the Cu^{II} in a four- or five-co-ordinate environment.[10,11] Similar effects should be manifest with low molecular weight complexes if the geometry of the Cu^{II} is favourable. It seemed to us relevant, therefore, to study redox processes involving square-planar and tetrahedral, as well as five-co-ordinate, Cu^{II} complexes.

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† No reprints available.

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The fully saturated macrocyclic (±)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azatetradecane ligand (tet-b) reacts with copper(II) salts in basic solution to form a blue complex which readily isomerizes into a red form. This isomerization can be prevented by rapid addition of acid, and the nature of the blue species has been investigated in some detail.[12] In the presence of chloride and perchlorate a binuclear, five-co-ordinate compound of the blue tet-b complex $[Cu_2(\text{tet-b})_2Cl](ClO_4)_3$ has been isolated and the crystal structure determined. The corresponding binuclear complexes with bromide and iodide do not form, and monomeric halide adducts $[Cu(\text{tet-b})Br]ClO_4$ and $[Cu(\text{tet-b})I]ClO_4$ have been isolated.[12] It has been concluded that blue $[Cu^{II}(\text{tet-b})]^{2+}$ is monomeric in aqueous solution, forming weak adducts with H_2O and halide ions. Studies on the Cr^{2+}, V^{2+}, and $[Ru(NH_3)_6]^{2+}$ reductions of $[Cu^{II}(\text{tet-b})X]^+$ complexes ($X^- = Cl^-$, Br^-, and thiourea) are reported in this paper.

EXPERIMENTAL

Reactants.—The tet-b ligand was prepared and purified by the method of Whimp and Curtis,[13] as modified by Warner and Busch.[14] Blue $[Cu^{II}(\text{tet-b})](ClO_4)_2$ [12] was prepared by treating the ligand with copper(II) perchlorate (G. F. Smith, Chemical Co.) in *ca*. 0.1M NaOH solution, followed by rapid quenching of the blue-to-red isomerization by the addition of 5M $HClO_4$. The product was isolated by concentrating the solution on a rotary evaporator to a quarter volume, and leaving it overnight at *ca*. 0 °C. It was recrystallized until a constant spectrum peak was obtained [λ 830 (ε 206 l mol^{-1} cm^{-1}) from 10^{-3}M $HClO_4$]. Analyses were as follows: Found: C, 35.3; H, 6.4; Cl, 12.9; Cu, 11.4. N, 9.9. Calc. for $[Cu(C_{16}H_{36}N_4)](ClO_4)_2$ assuming absence of H_2O: C, 35.1; H, 6.6; Cl, 13.0; Cu, 11.6; N, 10.2%. There was no loss in weight when the product was left over P_2O_5 *in vacuo* for 4 days. Analyses do not exclude the possibility of a co-ordinated H_2O.

Solutions of Cr^{2+} and V^{2+} perchlorate in dilute perchloric acid (*ca*. 1.0M) were prepared by electrolytic reduction (Hg pool electrode) of Cr^{III} and V^{IV} solutions. To prepare $[Ru(NH_3)_6]^{2+}$ a solution of $[Ru(NH_3)_6]Cl_3$ (*ca*. 10^{-3}M) in H_2O was reduced using a column of amalgamated zinc shot (*ca*. 65% conversion). The Ru^{II} was determined spectrophotometrically after the compound had been treated with an excess of the μ-superoxo-complex $[(NH_3)_5Co\cdot O_2\cdot Co(NH_3)_5]^{5+}$ [peak at 297 nm (ε 2.32×10^4 l mol^{-1} cm^{-1})].[15] *p*-Toluenesulphonic acid (Aldrich), hereafter Hpts, was recrystallized twice from H_2O (<70 °C). The Li salt was prepared by addition of Li_2CO_3 (B.D.H., Reagent Grade) and recrystallizing from H_2O. The acids HCl, HBr, and $HClO_4$ were AnalaR grade, LiCl (B.D.H., G.P.R. grade) was recrystallized twice from H_2O, and LiBr (G.P.R. grade) twice from ethanol. Thiourea (B.D.H., Lab Reagent) was recrystallized twice from H_2O and dried *in vacuo* over P_2O_5. Standard air-free techniques, syringes, rubber serum caps, and stainless-steel needles were used for all solutions of Cr^{2+}, V^{2+} (under N_2), and $[Ru(NH_3)_6]^{2+}$ (under argon).

Ion-exchange Separation of Products.—To a de-aerated (N_2) solution of $[Cu^{II}(\text{tet-b})]^{2+}$ (20 ml, 2×10^{-3}M) were added HCl (1 ml, 2M) and Cr^{2+} (4.5 ml, 9×10^{-3}M). The solution was left for 45 min at *ca*. 20 °C and then loaded onto a Dowex 50W-X12 (H^+ form) resin column (2.5 cm diam 3-cm long) in air. Excess of Cr^{2+} reactant was oxidized to dimeric (and polymeric) Cr^{III}. Neutral and anionic products were washed off the column with H_2O (20 ml). Elution with first 0.3M followed by 0.8M Hpts gave in the latter case a coloured fraction. No further bands were eluted with 3M-acid.

The same procedure was adopted with Br^- as for Cl^- except that, because of the decreased solubility of $[Cu^{II}(\text{tet-b})Br]^+$, the Cu^{II} concentration was 9×10^{-4}M and only 2 ml of Cr^{2+} was added. For the thiourea-assisted reaction $[Cu^{II}(\text{tet-b})]^{2+}$ was 2.3×10^{-3}M; thiourea (5 ml, 1M) and Cr^{2+} (0.8 ml, 5×10^{-2}M) were added. The only coloured fraction to be eluted was with 3M $HClO_4$, thiourea being a neutral ligand. A repeat experiment without Cu^{II} gave no mononuclear Cr^{III} product.

Stoicheiometry and Effect of Perchlorate.—The stoicheiometry as determined spectrophotometrically was close to 1 Cu^{II} : 2 Cr^{2+} for Cr^{2+} runs in 0.2M-$[ClO_4]^-$ solutions, and a precipitate of copper metal was observed at the bottom of optical cells. Even allowing for this stoicheiometry rate constants in ClO_4^- solutions increased *ca*. 50% as the $[ClO_4^-]$ increased from 0.002 to 0.20M. It was therefore decided to work with Hpts solution, $I = 0.20$M (Lipts) with near equivalent amounts of reactants, Cu^{II} in excess. Copper metal precipitated in all media when the reducing agent was in excess, due to the further reduction of the Cu^I product. Small amounts of perchlorate $[ClO_4^-] < 9 \times 10^{-3}$M introduced with reactants have no effect. The same procedure was adopted also with V^{2+}. Stoicheiometries were determined for each run according to the amount of oxidant consumed from spectrophotometric changes at 830 nm. In all cases the stoicheiometry was 1 : 1 with some (random) deviations of up to 10% which could be attributed to loss of reductant during the transference procedure. The spectrum of $[Cu^{II}(\text{tet-b})]^{2+}$ (2.5×10^{-4}M) with thiourea (0.5M) remained unchanged for >6 h at 60 °C in 0.2M Hpts.

Nature of Copper(I) *Product*.—The Cu^I product obtained in these studies does not give back $[Cu^{II}(\text{tet-b})]^{2+}$ spectra (red or blue isomer) on reoxidation. From spectra obtained the Cu^I product could be the aquo-ion Cu^+ and the reoxidized product Cu^{2+}. This implies tet-b dissociation from the initially generated $[Cu^I(\text{tet-b})]^+$ complex.

Kinetics.—Solutions were in Hpts, $I = 0.2$M (Lipts), $[ClO_4^-] \leqslant 9 \times 10^{-3}$M, with varying amounts of X^-. Reactions were monitored by conventional spectrophotometry (Unicam SP 500) at wavelengths 675 and *ca*. 830 nm, where the Cu^{II} is the strongest absorbant (see above). Second-order rate constants k_{obs} were obtained from the slope $(a_0 - b_0)k_{\text{obs}}/2.303$ of plots of $\log_{10}\{1 + (a_0 - b_0)(\Delta\varepsilon l/\Delta A)\}$ against time, where a_0 and b_0 are the initial concentrations of Cu^{II} and Cr^{2+}, $\Delta\varepsilon$ the change in absorption coefficients at the wavelength monitored, l the cell path-length, and ΔA the absorbance change. Runs were linear to >80% completion, except in the slower V^{2+} runs. With X^- = thiourea some hydrolysis of thiourea (to give H_2S) was detected.

Equilibrium Constants.—Solutions of $[Cu^{II}(\text{tet-b})]^{2+}$ (*ca*. 2×10^{-3}M) were made up at varying X^- concentrations; Cl^- (0—0.20M), Br^- (0—0.20M), and thiourea (0—0.50M), $[H^+] = 0.2$M. Spectra show no dependence on $[H^+]$ in the

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range 0.01—0.20M and it is assumed that the tet-b ligand remains quadridentate. Absorbance changes at 675 and/or 830 nm were fitted to equation (1) and K evaluated.

$$A = \frac{A_0 - A_\infty K[\mathrm{X}^-]}{1 + K[\mathrm{X}^-]} \qquad (1)$$

Agreement of data obtained at the two wavelengths was satisfactory (±7%). Values (l mol^{-1}) obtained at 675 nm are 8.1 ± 0.7 (Cl$^-$), 11.3 ± 0.2 (Br$^-$), and 1.9 ± 0.4 (thiourea).

TABLE 1

Rate constants for the Cr^{2+} reduction of $[Cu^{II}(tet\text{-}b)]^{2+}$ in the presence of chloride at 25 °C, I = 0.20M (Lipts), λ 845 nm

[H$^+$]	[Cl$^-$]	10^4[Cu^{II}]	10^4[Cr^{2+}]	k_{obs}
M	M	M	M	l mol^{-1} s^{-1}
0.20	0.025	4.59	3.06	4.84
0.10	0.025	4.54	3.05	4.11
0.025	0.025	4.54	3.29	4.59
0.20	0.033	4.59	3.17	6.01
0.20	0.050	4.59	3.28	7.26
0.20	0.075	4.59	2.65	9.33
0.20	0.10	4.63	3.04	10.6
0.20	0.20	4.92	2.27	14.0
0.20	0.20	3.93	3.35	13.1
0.20	0.20	7.86	7.54	13.9
0.20	0.20	6.18	3.76	12.4
0.20	0.20	4.15	3.58	12.4
0.15	0.20	5.01	2.61	12.9
0.10	0.20	5.03	3.18	13.1
0.05	0.20	5.03	3.38	12.3
0.05	0.20	4.25	3.80	14.0 [a]

[a] λ 675 nm.

The temperature dependence of K(l mol^{-1}) was investigated; X = Cl$^-$, K = 12.6 ± 2.9 (40 °C), 15.2 ± 2.1 (50 °C), and 18.8 ± 1.6 (60 °C). Spectra obtained for $[Cu^{II}(tet\text{-}b)]^{2+}$ in the presence of different X$^-$ are shown in Figure 1. Peak positions (nm) and absorption coefficients (l mol^{-1} cm^{-1}) are $[Cu^{II}(tet\text{-}b)Cl]^+$ 672 (274), 840 (271); $[Cu^{II}(tet\text{-}b)Br]^+$, 666 (381), 830 (276); and $[Cu^{II}(tet\text{-}b)(thiourea)]^{2+}$ *ca.* 675 (525), from the above treatment.

TABLE 2

Rate constants for the Cr^{2+} reduction of $[Cu^{II}(tet\text{-}b)]^{2+}$ in the presence of bromide at 25 °C, I = 0.20M (Lipts), λ 830 nm

[H$^+$]	[Br$^-$]	10^4[Cu^{II}]	10^4[Cr^{2+}]	k_{obs}
M	M	M	M	l mol^{-1} s^{-1}
0.20	0.025	4.17	2.61	3.71
0.20	0.033	4.17	1.75	4.80
0.20	0.050	4.40	3.80	7.06
0.20	0.050	2.08	0.90	6.87
0.20	0.050	2.50	2.02	6.98
0.20	0.050	4.40	3.80	6.80 [a]
0.050	0.050	4.40	3.80	6.86 [a]
0.050	0.050	4.44	3.80	7.25 [b]
0.050	0.050	6.66	3.80	6.28
0.050	0.050	2.22	3.80	6.64
0.20	0.075	4.19	3.65	8.86
0.20	0.100	4.25	3.08	9.94
0.20	0.100	4.19	3.82	9.65 [c]

[a] $[ClO_4^-] = 9.1 \times 10^{-3}$M. [b] $[ClO_4^-] = 2.3 \times 10^{-3}$M. [c] λ 675 nm.

RESULTS

Cr^{2+} *as Reductant.*—Reactions were studied at 25 °C, I = 0.20M (Lipts). Conversion of $[Cu^{II}(tet\text{-}b)]^{2+}$ to $[Cu^{II}(tet\text{-}b)X]^+$ is incomplete for the range of reactant concentrations investigated, [Cl$^-$] = 0.025—0.20M, [Br$^-$] = 0.025—0.10M, and [thiourea] = 0.05—0.50M. In the absence of added X$^-$ ligand, [H$^+$] = 0.20M, negligible (≤2%) Cr^{2+} (3.2×10^{-4}M) reduction of $[Cu^{II}(tet\text{-}b)]^{2+}$ (4.5×10^{-4}M) occurs in 20 h. For runs with X$^-$ added the Cr^{III} products were separated by an ion-exchange procedure (>90% retrieval), and identified spectrophotometrically as $CrCl^{2+}$, $\lambda_{max.}$ 428 and 608 nm, $CrBr^{2+}$ $\lambda_{max.}$ 430 and 615 nm (in good agreement with literature values),[16] and $[Cr(thiourea)]^{3+}$, $\lambda_{max.}$ 255, 420, and 585 nm. By using an excess of Cu complex further reduction of the Cu^I product was avoided and 1 : 1 stoicheiometries were observed. Second-order rate constants k_{obs} (Tables 1—3) are independent of [H$^+$] in the range 0.01—0.20M investigated.

$$k_{obs} = \frac{k_X K[\mathrm{X}^-]}{1 + K[\mathrm{X}^-]} \qquad (2)$$

The dependence of k_{obs} on [X$^-$] [equation (2)] was shown to be valid in each case by plot-

TABLE 3

Rate constants for the Cr^{2+} reduction of $[Cu^{II}(tet\text{-}b)]^{2+}$ in the presence of thiourea at 25 °C, I = 0.20M (Lipts), λ 830 nm

[H$^+$]	[Thiourea]	10^4[Cu^{II}]	10^4[Cr^{2+}]	k_{obs}
M	M	M	M	l mol^{-1} s^{-1}
0.20	0.050	4.20	2.10	8.7
0.20	0.050	6.30	4.34	7.2
0.20	0.050	8.50	5.60	8.9
0.20	0.075	6.40	3.50	10.8
0.20	0.075	5.19	2.66	11.2
0.01	0.10	6.40	4.00	13.9
0.10	0.10	6.20	4.30	14.5
0.20	0.10	6.20	4.20	14.5
0.20	0.15	4.26	1.50	19.9
0.20	0.20	6.50	3.90	23.9
0.20	0.20	3.46	1.23	25.9
0.20	0.50	3.46	0.75	42.0

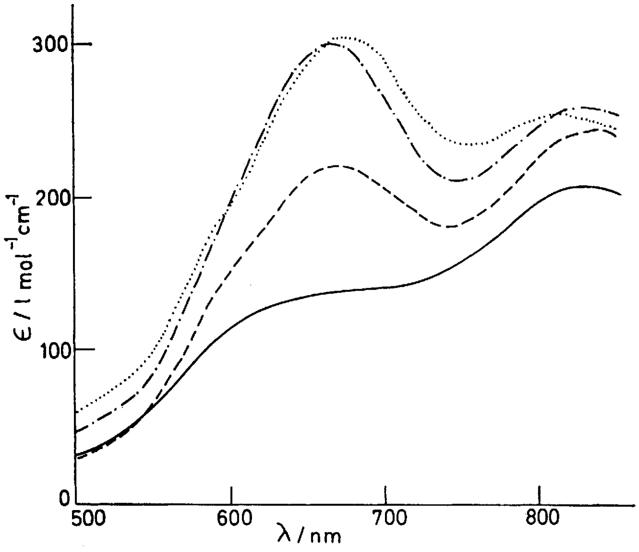

FIGURE 1 Aqueous solution spectra of $[Cu^{II}(tet\text{-}b)]^{2+}$ in the presence of: 0.2M-Hpts (——); 0.2M-HCl (60%) (— —); 0.2M-HBr (70%) (— · — · —), and 0.5M-thiourea (48%) (· · · ·) at *ca.* 25 °C. Approximate percentage complexation to yield $[Cu^{II}(tet\text{-}b)X]^+$ as calculated from spectrophotometric equilibrium constants is indicated in brackets

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[16] P. Moore and F. Basolo, *Inorg. Chem.*, 1965, **4**, 1670.

ting $1/k_{obs}$ against $1/[X^-]$ (Figure 1). Values of k_X and K were obtained from a weighted $(1/y^2)$ non-linear least-squares computer fit,[17] and are shown in Table 6 below.

V^{2+} *as Reductant.*—Full studies were made of the reduction of $[Cu^{II}(tet\text{-}b)X]^+$ ($X^- = Cl^-$ and thiourea). No reaction of V^{2+} (2.7×10^{-4}M) with $[Cu^{II}(tet\text{-}b)]^{2+}$ (5×10^{-4}M), [Hpts] = 0.20M, was observed (λ 830 nm), in the absence of added X^-, within 6 h. Rate constants k_{obs} (Tables 4 and 5) fit a dependence of the form (2). Values of k and K_X are listed in Table 6. From the temperature dependence 40—60 °C activation parameters for k_X and thermodynamic parameters for K were obtained using a non-linear least-squares fit ($1/y^2$ weighting)[17] (Table 7). Errors applying for X^- = thiourea are large due to the relatively small K value. Two runs only were carried out with $X^- = Br^-$ owing to the slowness of the reaction.

TABLE 4

Rate constants for the V^{2+} reduction of $[Cu^{II}(tet\text{-}b)]^{2+}$ in the presence of chloride, I = 0.20M (Lipts), λ 845 nm

Temp. (θ_c/°C)	$[H^+]$ M	$[Cl^-]$ M	$10^4[Cu^{II}]$ M	$10^4[V^{2+}]$ M	k_{obs} l mol^{-1} s^{-1}
40.0	0.20	0.05	4.82	2.81	0.046
	0.20	0.065	5.17	2.81	0.065
	0.20	0.10	5.17	2.81	0.071
	0.20	0.15	5.22	2.81	0.089
	0.20	0.20	5.22	2.81	0.096
50.0	0.20	0.05	5.08	2.81	0.104
	0.20	0.075	5.08	2.81	0.117
	0.20	0.10	5.08	2.81	0.135
	0.20	0.15	4.99	2.81	0.150
	0.20	0.20	5.35	2.84	0.160
	0.20	0.20	7.13	4.26	0.158
	0.20	0.20	2.72	1.41	0.160
	0.02	0.20	5.40	2.82	0.160
	0.10	0.20	5.42	2.84	0.160
60.0	0.20	0.05	4.81	2.81	0.216
	0.20	0.075	4.81	2.81	0.243
	0.20	0.10	5.17	2.81	0.261
	0.20	0.15	5.17	2.81	0.295
	0.20	0.20	5.22	2.81	0.311

TABLE 5

Rate constants for the V^{2+} reduction of $[Cu^{II}(tet\text{-}b)]^{2+}$ in the presence of thiourea, I = 0.20M (Lipts), λ 830 nm

Temp. (θ_c/°C)	$[H^+]$ M	[Thiourea] M	$10^4[Cu^{II}]$ M	$10^4[V^{2+}]$ M	k_{obs} l mol^{-1} s^{-1}
40.0	0.20	0.10	4.95	2.83	0.0072
	0.20	0.20	4.95	2.83	0.012
	0.20	0.30	4.95	2.83	0.018
	0.20	0.40	4.95	2.83	0.021
	0.20	0.50	4.95	2.83	0.028
50.0	0.20	0.10	6.47	4.50	0.021
	0.20	0.20	4.95	2.83	0.022
	0.20	0.30	4.95	2.83	0.038
	0.20	0.40	4.95	2.83	0.041
	0.20	0.50	3.20	1.41	0.053
	0.20	0.50	5.01	2.83	0.052
	0.20	0.50	6.21	4.25	0.048
	0.20	0.50	2.88	0.71	0.052
	0.10	0.50	5.01	2.83	0.052
	0.010	0.50	5.01	2.83	0.052
60.0	0.20	0.10	4.95	2.83	0.054
	0.20	0.20	4.95	2.83	0.063
	0.20	0.30	4.95	2.83	0.077
	0.20	0.40	4.95	2.83	0.090
	0.20	0.50	5.01	2.83	0.110
	0.20	0.50	8.65	6.37	0.150

$[Ru(NH_3)_6]^{2+}$ *as Reductant.*—No absorbance changes were observed (λ 830 nm) in 2.5 h at 20 °C with $[Cu^{II}(tet\text{-}b)^{2+}] = 8.6 \times 10^{-4}$M, $[Ru(NH_3)_6{}^{2+}] = 3.5 \times 10^{-4}$M, $[H^+]$ = *ca.* 3×10^{-4}M, $[Cl^-]$ = 0.20M, I = 0.20M. The $[Ru(NH_3)_6{}^{2+}]$ in the reaction solution was redetermined after this time and found to be >90% of the inital value. For the conditions investigated >50% of the tet-b complex is present as $[Cu^{II}(tet\text{-}b)Cl]^+$. It is concluded that k_X is $\leqslant 10^{-3}$ l mol^{-1} s^{-1}.

DISCUSSION

On addition of Cl^-, Br^-, and thiourea to solutions of $[Cu^{II}(tet\text{-}b)]^{2+}$, spectrophotometric changes (Figure 1) indicate inner-sphere complex formation. The equation for complexing may be expressed as in (3), where all

$$[Cu^{II}(tet\text{-}b)]^{2+} + X^- \rightleftharpoons [Cu^{II}(tet\text{-}b)X]^+ \quad (3)$$

three ligands are designated as X^-. Spectrophotometric studies are consistent with 1 : 1 complexing and yield equilibrium constants (l mol^{-1}) at 25 °C, I = 0.20M (Lipts), of 8.1 (Cl^-), 11.3 (Br^-), and 1.9 (thiourea). Values obtained from the kinetic treatment (Table 6) are in satisfactory agreement. On the basis of an *X*-ray crystallographic study already reported,[12] distorted trigonal bipyramidal geometries seem likely. Bonding of thiourea to the Cu is probably at the S atom.

TABLE 6

Summary of equilibrium constants K for the formation of $[Cu^{II}(tet\text{-}b)X]^+$ from $[Cu^{II}(tet\text{-}b)]^{2+}$ (from kinetics) and rate constant k_X for the reduction of $[Cu^{II}(tet\text{-}b)X]^+$, I = 0.20M (Lipts)

Reductant	Oxidant	K(25 °C) l mol^{-1}	k_X (25 °C) l mol^{-1} s^{-1}
Cr^{2+}	$[Cu^{II}(tet\text{-}b)Cl]^+$	14 ± 1.0	17.9 ± 0.6
Cr^{2+}	$[Cu^{II}(tet\text{-}b)Br]^+$	9.1 ± 1.6	21.4 ± 2.5
Cr^{2+}	$[Cu^{II}(tet\text{-}b)(thiourea)]^{2+}$	2.2 ± 0.31	81 ± 10
V^{2+}	$[Cu^{II}(tet\text{-}b)Cl]^+$	*ca.* 6 [b]	0.055 [a]
V^{2+}	$[Cu^{II}(tet\text{-}b)Br]^+$		*ca.* 0.03 [c]
V^{2+}	$[Cu^{II}(tet\text{-}b)(thiourea)]^{2+}$	*ca.* 1 [d]	0.020 [a]
$Ru(NH_3)_6{}^{2+}$	$[Cu^{II}(tet\text{-}b)Cl]^+$		$<10^{-3}$ [e]

[a] Extrapolated from data 40—60 °C. [b] Extrapolated value, large error. Values at other temperatures 11.7 (40 °C), 17.7 (50 °C), 25.9 (60 °C). [c] Two runs only at 50 °C; rate constants k in the range 0.024—0.039 l mol^{-1} s^{-1} obtained assuming K = 15—25 l mol^{-1}. [d] Extrapolated value, large error. Values at other temperatures 1.6 (40 °C), 2.2 (50 °C), and 2.9 (60 °C). [e] At 20 °C; extrapolated value for V^{2+} reduction of $[Cu^{II}(tet\text{-}b)Cl]^+$ at 20 °C is 0.04 l mol^{-1} s^{-1}.

TABLE 7

Summary of activation and thermodynamic parameters for k_X and K respectively obtained for the V^{2+} reduction of $[Cu^{II}(tet\text{-}b)X]^+$ complexes

Reaction	Term	ΔH kcal mol^{-1}	ΔS cal K^{-1} mol^{-1}
$X^- = Cl^-$	k_X	9.9 ± 1.2 [a]	−31.0 ± 3.8 [a]
	K	8.2 ± 3.2 [b]	+31.0 ± 9.8 [b]
X^- = thiourea	k_X	12 ± 5 [a]	−27 ± 15 [a]
	K	6.6 ± 7.8 [b]	22 ± 24 [b]

[a] Activation parameters. [b] Thermodynamic parameters.

Without addition of X^- little or no reduction of Cu^{II} occurs and upper limits of rate constants are $<10^{-4}$ l mol^{-1} s^{-1} (Cr^{2+}, 25 °C) and $<5 \times 10^{-4}$ l mol^{-1} s^{-1} (V^{2+}, 50 °C).

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[17] R. H. Moore and R. K. Zeigler, Los Alamos Report LA2367 and *Addenda*, Los Alamos Scientific Laboratory, Los Alamos, N.M., U.S.A., 1959.

No acid dissociation of $[Cu^{II}(tet\text{-}b)H_2O]^{2+}$ was detected at the acid pH values investigated, and a $pK_a > 7$ is implied. The reluctance of an H_2O ligand to provide a site for inner-sphere electron transfer has previously been noted.[18] From the limiting rate constants obtained it is concluded that outer-sphere processes are likewise unfavourable.

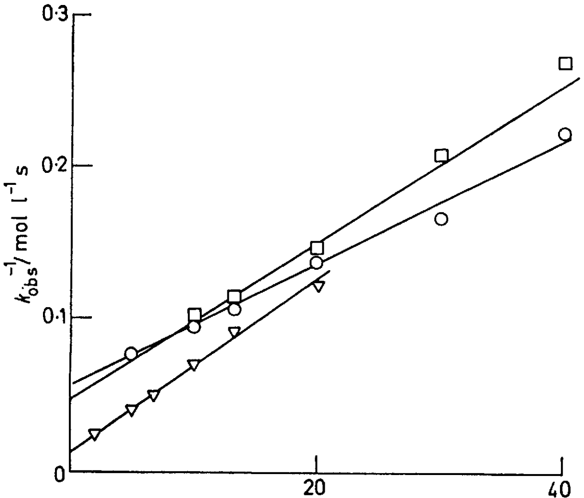

FIGURE 2 Illustrating the dependence of $1/k_{obs}$ on $1/[X^-]$ for Cr^{2+} reduction of $[Cu^{II}(tet\text{-}b)]^{2+}$ in the presence of $X^- = Cl^-$ (○), Br^- (□), and thiourea (▽) at 25 °C, I = 0.20M (Lipts)

Reduction of the $[Cu^{II}(tet\text{-}b)X]^+$ complexes by Cr^{2+} gives CrX^{2+} products which were separated by ion-exchange chromatography and identified spectrophotometrically. With X^- = thiourea the Cr^{III} product has absorption peaks at 420 and 585 nm and by comparison with visible spectra of other penta-aquochromium(III) complexes with S-bonded ligands, *e.g.* $[CrSH]^{2+}$ and $[Cr(SC_6H_4NH_3^+)]^{3+}$,[19] is here assigned an S-bonded $[CrSC(NH_2)_2]^{3+}$ structure. The 420 nm peak would have been expected in the region <400 nm if the ligand had been N-bonded. The order of effectiveness of different X^- ligands in assisting electron transfer as determined by rate constants (l mol^{-1} s^{-1}) is Cl^- (17.9), Br^- (21.4), and thiourea (81). Although the differences are not particularly large the preference for S-atom bridging is noted. With Co^{III} oxidants, S-atom sites are less efficient than halide ions in Cr^{2+} reductions.[20] The overall equation may be written as in (4).

$$[Cu^{II}(tet\text{-}b)X]^+ + Cr^{2+} \longrightarrow CrX^{2+} + [Cu^{I}(tet\text{-}b)]^+ \quad (4)$$

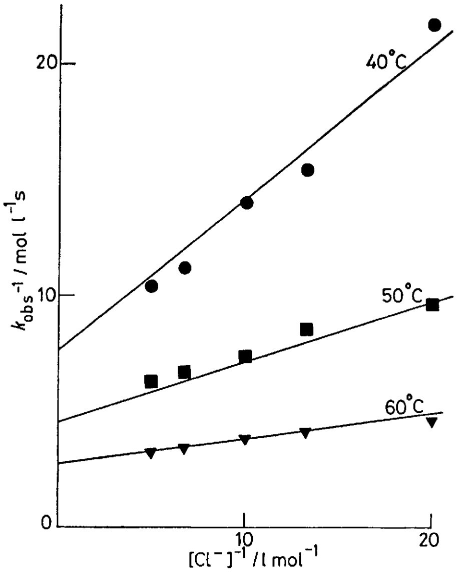

FIGURE 3 Dependence of $1/k_{obs}$ on $1/[Cl^-]$ for V^{2+} reduction of $[Cu^{II}(tet\text{-}b)]^{2+}$, I = 0.20M (Lipts)

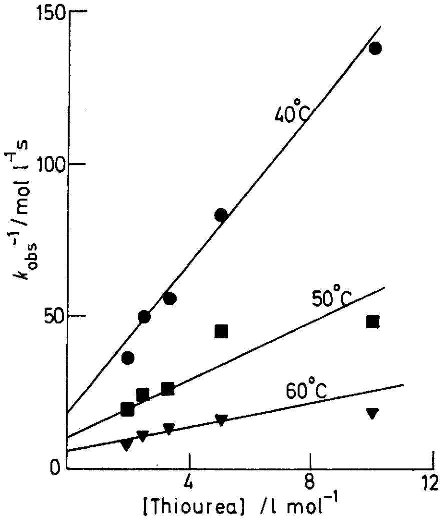

FIGURE 4 Dependence of $1/k_{obs}$ on 1/[thiourea] for the V^{2+} reduction of $[Cu^{II}(tet\text{-}b)]^{2+}$, I = 0.20M (Lipts)

Addition of a suitable oxidant ($[Fe(CN)_6]^{3-}$, $[IrCl_6]^{2-}$, or air) does not regenerate $[Cu^{II}(tet\text{-}b)]^{2+}$ complexes, however, and rapid aquation of the $[Cu^{I}(tet\text{-}b)]^+$ product is implied.

One advantage of using V^{2+} as a reductant is the ease with which it can resort to an outer-sphere pathway when an inner-sphere pathway is less favourable. Previous studies have indicated that V^{2+} is reluctant to utilize Cl^- and Br^- as a bridging ligand for inner-sphere electron transfer. Thus V^{2+} reductions of $[Co(NH_3)_5X]^{2+}$ with $X^- = Cl^-$ and Br^- (unlike $X^- = F^-$) proceed by an outer-sphere mechanism.[21] There seemed every likelihood therefore that reduction of $[Cu^{II}(tet\text{-}b)Cl]^+$ would be outer-sphere. This is excluded by the $[Ru(NH_3)_6]^{2+}$ study, rate constant $<10^{-3}$ l mol^{-1} s^{-1} for reduction of $[Cu^{II}(tet\text{-}b)Cl]^+$, which from the correlation of rate constants for the $[Ru(NH_3)_6]^{2+}$ (k_{Ru}) and V^{2+} (k_V) reductions

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[18] D. L. Toppen and R. G. Linck, *Inorg. Chem.*, 1971, **10**, 2635.

[19] L. E. Asher and E. Deutsch, *Inorg. Chem.*, 1972, **11**, 2927.

[20] *E.g.* R. H. Prince and M. G. Segal, *J.C.S. Chem. Comm.*, 1976, 100.

[21] M. R. Hyde, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, 1973, 2730.

of common oxidants, a series of Co^{III} complexes gives (5).*

$$\log k_V = 0.81 \log k_{Ru} - 0.64 \qquad (5)$$

On the basis of this correlation, k_V for the outer-sphere V^{2+} reduction of $[Cu^{II}(\text{tet-b})Cl]^+$ is *ca.* 10^{-3} l mol^{-1} s^{-1}. The observed rate constant (0.055 l mol^{-1} s^{-1}) at 25 °C is far in excess of this value. It is concluded that the V^{2+} reaction is inner-sphere, with at the most a small outer-sphere contribution. The kinetic data for the V^{2+} reduction of $[Cu^{II}(\text{tet-b})Cl]^+$ would seem to preclude a substitution-controlled process (k in the range 2—50 l mol^{-1} s^{-1}, $\Delta H^\ddagger$ = *ca.* 12 kcal mol^{-1}, $\Delta S^\ddagger$ = *ca.* −17 cal K^{-1} mol^{-1}).[23] On this evidence it is possible that the V^{2+} reduction is an inner-sphere electron-transfer controlled process, a category of reaction that has not previously been assigned with certainty.[24] A similar assignment is made also for the V^{2+} reduction of $[Cu^{II}(\text{tet-b})(\text{thiourea})]^{2+}$.

To summarize, Cu^{II} complexes of the macrocyclic tet-b ligand with Cl^-, Br^-, and thiourea occupying the fifth co-ordination position will undergo inner-sphere Cr^{2+} reduction, but with V^{2+} and $[Ru(NH_3)_6]^{2+}$ are unable to utilize effectively an outer-sphere pathway. The V^{2+} would appear to utilize instead an unfavourable inner-sphere route. With regard to Cu^I–Cu^{II} aquo-ion redox interconversions it has already been concluded that reorganization energy requirements are too demanding to permit a ready outer-sphere reaction. The same would seem to apply for the five-co-ordinate complexes described here.

We thank the S.R.C. for financial support (M. G. S.) and the Kuwait Government for a scholarship (to N. A.-S).

[7/077 *Received, 17th January, 1977*]

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* Correlation of rate constants k_V and k_{Ru} for reduction of 28 Co^{III} complexes. Five Pt^{IV} oxidants give a similar correlation.[22]

[22] T. D. Hand, Ph.D. Thesis, University of Leeds, 1976.

[23] N. Sutin, *Accounts Chem. Res.*, 1968, **1**, 225.

[24] See, however, J. C. Chen and E. S. Gould, *J. Amer. Chem. Soc.*, 1973, **95**, 5339, for a possible example.