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Kinetics and Mechanism of the Redistribution Reactions of the 5-Coordinate Gold(III) Complexes $[Au(N-N)(CN)_2X]$

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The square-pyramidal, 5-coordinate species $[Au(N-N)(CN)_2X]$ (N–N = 1,10-phenanthroline, 5-methyl-1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline; X = Cl, Br), formed by the reaction between N–N and *trans*-$K[Au(CN)_2X_2]$, undergo, in solution, a very rapid intramolecular exchange of the apical and basal nitrogens together with a slow reaction that gives $[Au(N-N)(CN)_2]^+$, *trans*-$[Au(CN)_2X_2]^-$, and N–N as products. The reaction is first order in 5-coordinate complex, and the proposed mechanism is as follows: $[Au(N-N)(CN)_2X] \rightarrow [Au(N-N)(CN)_2]^+ + X^-$ (slow); $[Au(N-N)(CN)_2X] + X^- \rightarrow$ *trans*-$[Au(CN)_2X_2]^- +$ N–N (fast). The rate constant for this reaction depends upon the nature of N–N (the hindered 2,9-dimethyl-1,10-phenanthroline complex reacting very slowly) and the solvent (reactions in dimethyl sulfoxide or in aqueous dimethylformamide are faster than those in dimethylformamide, *sym*-dichloroethane, and butanone). In general, the differences in the reactivity of the chloro and bromo species are not large and depend upon the nature of the substrate.

Introduction

The characteristic associatively activated pathway for ligand substitution in 4-coordinate planar d^8 metal complexes requires a 5-coordinate transition state, and information gained from stable or relatively long-lived 5-coordinate systems can be used to advance understanding of the transient species. In Au(III) chemistry 5-coordinate or even 6-coordinate species are well-known in the solid state, for example $[Au(diars)_2I_2]I$,[3] $[Au(diars)_2I]^{2+}$[4] [diars = *o*-phenylenebis(dimethylarsine)], and $[Au(N-N)X_3]$, where X = Cl or Br and N–N = 2,2′-biquinolyl,[5] 2,9-dimethyl-1,10-phenanthroline,[6] or 2-(2-pyridyl)quinoline.[7] The simplest members of this series (where N–N = 2,2′-bipyridyl[8,9] and 1,10-phenanthroline[10]) appear to undergo ready redistribution in solution, where it has been shown that $[Au(N-N)X_3]$ gives $[Au(N-N)X_2]^+ + [AuX_4]^- +$ N–N (N–N = 1,10-phenanthroline,[10] 2,2′-bipyridyl;[9] X = Cl, Br).

These redistributions are quite rapid, and in order to slow down the reactions, we examined the species formed when *trans*-$[Au(CN)_2X_2]^-$ (X = Cl, Br) reacts with 1,10-phenanthroline and similar ligands. In this substrate X provides a labile entrance for the formation of a 5-coordinate species; and, provided there is no facile rearrangement, return to a 4-coordinate species would require the displacement of the inert CN^-. Complexes of the type $[Au(N-N)(CN)_2X]$ were indeed isolated as monomeric species, and the single-crystal X-ray diffraction study of the complex where N–N = 1,10-phenanthroline and X = Br showed it to be square pyramidal 5-coordinate with the chelate spanning apical and basal sites and the two cyanides ligands trans.[11]

This paper reports the nature and the kinetics of the redistribution reactions of these complexes in a variety of solvents.

Experimental Section

Materials. $HAuCl_4·3H_2O$ was purchased from Englehard. All other chemicals were reagent grade products purchased from either Aldrich or Hoechst. *trans*-$K[Au(CN)_2Cl_2]·H_2O$ was prepared by the method of Cattalini,[12] and *trans*-$K[Au(CN)_2Br_2]·3H_2O$ was prepared by the method of Blomstrand.[13]

Dicyanobromo(1,10-phenanthroline)gold(III)–dimethylformamide was obtained by the method reported elsewhere.[11]

The ^1H NMR spectrum in $[^2H_7]$dimethylformamide has peaks at δ 1.74 (dd, phen-2,9, 2 H, $^3J_{2,3} = {}^3J_{9,8} = 5.0$ Hz, $^4J_{2,4} = {}^4J_{9,7} = 1.44$ Hz), 1.12 (dd, phen-4,7, 2 H, $^3J_{4,3} = {}^3J_{7,8} = 8.15$ Hz, $^4J_{4,5} = {}^4J_{4,2} = {}^4J_{7,6} = {}^4J_{7,9} = 1.44$ Hz), 0.44 (s, phen-5,6, 2 H), and 0.36 (m, phen-3,8, 2 H).

Dicyanobromo(5-methyl-1,10-phenanthroline)gold(III) was obtained by a similar method. A solution of 5-methyl-1,10-phenanthroline (194 mg; 1 mmol) in methanol (1 cm^3) was added to one of *trans*-$K[Au(CN)_2Br_2]·3H_2O$ (502 mg; 1.0 mmol) in water (20 cm^3) at 0 °C, with stirring. The product precipitated immediately and was filtered off, washed with cold water, and dried under vacuum. Yield: 0.52 g (90%). The compound was obtained as pale yellow crystals (without DMF of crystallization) on recrystallizing from DMF/Et_2O.

Anal. Calcd for $C_{15}H_{10}N_4AuBr$: C, 34.4; H, 1.93; N, 10.7; Br, 15.3. Found: C, 34.7; H, 2.02; N, 10.8; Br, 15.4.

Characteristic IR peaks: 2181 m (ν_{CN}), 458 m (ν_{Au-C}), 428 m (δ_{Au-C-N}), 261 cm^{-1} (ν_{Au-Br}).

^1H NMR: δ 1.77 (dd, phen-9, 1 H, $^3J_{9,8} = 5.05$ Hz, $^4J_{9,7} = 1.35$ Hz), 1.63 (dd, phen-2, 1 H, $^3J_{2,3} = 5.05$ Hz, $^4J_{2,4} = 1.41$ Hz), 1.10 (dd, phen-7, 1 H, $^3J_{7,8} = 8.39$ Hz, $^4J_{7,6} = 1.51$ Hz), 1.03 (dd, phen-4, 1 H, $^3J_{4,3} = 8.39$ Hz, $^4J_{4,2} = 1.41$ Hz), 0.42 (s, phen-6, 1 H), 0.29 (m, phen-3,8, 2 H), −5.07 (s, 5-Me, 3 H).

Dicyanochloro(1,10-phenanthroline)gold(III) was prepared similarly by using 1,10-phenanthroline (180 mg; 1 mmol) in methanol (1 cm^3) and *trans*-$K[Au(CN)_2Cl_2]·H_2O$ (377 mg; 1 mmol) in water (20 cm^3). The creamy-white product (90% yield) was purified as before.

Anal. Calcd for $C_{14}H_8N_4AuCl$: C, 36.2; H, 1.74; N, 12.05; Cl, 7.63. Found: C, 36.5; H, 1.78; N, 11.9; Cl, 7.92.

Characteristic IR peaks: 2180 (ν_{CN}), 461 (ν_{Au-C}), 423 (δ_{Au-C-N}), 361 cm^{-1} (ν_{Au-Cl}).

Dicyanochloro(5-methyl-1,10-phenanthroline)gold(III) was prepared similarly in 95% yield.

Anal. Calcd for $C_{15}H_{10}N_4AuCl$: C, 37.6; H, 2.10; N, 11.7; Cl, 7.41. Found: C, 37.5; H, 2.07; N, 11.8; Cl, 7.45.

Characteristic IR peaks: 2180, 2162 (ν_{CN}), 455, 445 (ν_{Au-C}), 422 (δ_{Au-C-N}), 362 cm^{-1} (ν_{Au-Cl}).

Dicyanochloro(2,9-dimethyl-1,10-phenanthroline)gold(III). Attempts to prepare this complex by the method reported above invariably led to a compound that behaved as a 1:1 electrolyte in DMF and that proved to be $[N-NH]^+[Au(CN)_2Cl_2]^-$. The method of Robinson and Sinn[6] was used instead. 2,9-Dimethyl-1,10-phenanthroline (208 mg; 1 mmol), dissolved in a mixture of methanol and benzene (2/1 v/v) (15 cm^3), was added slowly to a stirred solution of *trans*-$K[Au(CN)_2Cl_2]·H_2O$ (377 mg; 1 mmol) in methanol (10 cm^3). The microcrystalline product slowly precipitated and was filtered off, washed with methanol and diethyl ether, and air-dried. Yield: 300 mg (61%).

Anal. Calcd for $C_{16}H_{12}N_4AuCl$: C, 39.0; H, 2.44; N, 11.4; Cl, 7.20. Found: C, 39.1; H, 2.44; N, 11.3; Cl, 7.18.

Characteristic IR peaks: 2180 (ν_{CN}), 453 (ν_{Au-C}), 427 (δ_{Au-C-N}), 357 cm^{-1} (ν_{Au-Cl}).

Dicyano(1,10-phenanthroline)gold(III) Perchlorate. $[Au(phen)(CN)_2Cl]$ (0.464 g; 1 mmol) was dissolved in DMF (10 cm^3), and the yellow solution was heated at 50 °C until the conductivity changed no further (ca. 1 h) and then saturated with $LiClO_4$. On addition of water (20 cm^3) the product started to separate, and precipitation was completed at 0 °C within a few hours. The product was filtered off and washed with water, methanol, and diethyl ether. The filtrate was clear and colorless.

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Anal. Calcd for $C_{14}H_8N_4AuClO_4$: C, 31.2; H, 1.51; N, 10.60; Cl, 6.71. Found: C, 31.1; H, 1.43; N, 10.30; Cl, 7.06.

Characteristic IR peaks: 2185 (ν_{CN}), 470, 480 (ν_{Au-C}), 430 cm^{-1} (δ_{Au-C-N}).

Conductance of a 1.0×10^{-3} mol dm^{-3} solution in DMF at 25 °C is 60 Ω^{-1} mol^{-1} cm^2.

^1H NMR: δ 1.76 (dd, phen-2,9, 2 H, $^3J_{2,3} = {}^3J_{9,8} = 5.35$ Hz, $^4J_{2,4} = {}^4J_{9,7} = 1.22$ Hz), 1.51 (dd, phen-4,7, 2 H, $^3J_{4,3} = {}^3J_{7,8} = 8.30$ Hz, $^4J_{4,5} = {}^4J_{4,2} = {}^4J_{7,6} = {}^4J_{7,9} = 122$ Hz), 0.61 (m, phen-5,6, 2 H + phen-3,8, 2 H).

The same product can be obtained on starting from $[Au(phen)(CN)_2Br]$.

Product A. A solution of $[Au(phen)(CN)_2Br]$ in DMF was heated at 50 °C until there was no further change in conductance. Water was added drop by drop until the solution become cloudy, and the mixture was set aside to crystallize at 0 °C. Fine red crystals formed and were filtered off, washed with water, methanol, and diethyl ether, and dried.

Anal. Calcd for $C_{12}H_8N_3AuBr_2$: C, 28.4; H, 1.43; N, 7.46; Br, 28.3; Calcd for $C_{13}H_8N_4AuBr$: C, 33.0; H, 1.58; N, 11.0; Br, 15.7. Found: C, 31.6; H, 1.52; N, 10.24; Br, 18.0. Calcd for a mixture containing 82% $C_{13}H_8N_4AuBr$ and 18% $C_{12}H_8N_3AuBr_2$: C, 32.0; H, 1.55; N, 10.3; Br, 18.2.

Conductance of a 1.0×10^{-3} mol dm^{-3} solution (assuming 1 mol contains 1 mol of Au) in DMF at 25 °C is 38 Ω^{-1} mol^{-1} cm^2.

Compound B. A solution of $[Au(phen)(CN)_2Br]$ in DMF was allowed to reach its equilibrium conductance and then treated with an equal volume of water. A yellow-orange microcrystalline precipitate separated, leaving a colorless mother liquor, and was filtered off, washed with water, methanol, and ether, and air-dried.

Anal. Calcd for $C_{14}H_8N_4AuBr$: C, 33.0; H, 1.57; N, 11.0; Br, 15.7. Found: C, 32.2; H, 1.48; N, 10.7; Br, 15.1.

Attempts to recrystallize this material invariably yield crystals of product A.

Conductance of a 1.0×10^{-3} mol dm^{-3} solution in DMF at 25 °C is 33 Ω^{-1} mol^{-1} cm^2 and increases slightly with time. Conductance of a 1.0×10^{-3} mol dm^{-3} solution in CH_3NO_2 is 50 Ω^{-1} mol^{-1} cm^2 (cf. 75–100 Ω^{-1} mol^{-1} cm^2 for a 1:1 electrolyte).

Compound C. A solution of $[Au(phen)(CN)_2Cl]$ in DMF was kept at 50 °C for 2 days and then cooled. On addition of diethyl ether, a yellow microcrystalline material separated and was filtered off, washed with water, methanol, and diethyl ether, and air-dried.

Anal. Calcd for $C_{12}H_8N_4AuCl$: C, 36.2; H, 1.72; N, 12.05; Cl, 7.63. Found: C, 35.6; H, 1.75; N, 11.9; Cl, 8.0.

The molar conductance of a 2.0×10^{-3} mol dm^{-3} solution in DMF at 25 °C is 27 Ω^{-1} mol^{-1} cm^2.

The same material is obtained when a methanolic solution of the 5-coordinate starting material is heated under reflux for 40 min.

Characteristic IR peaks: 2180 (doublet) (ν_{CN} coordinated), weak signal at 2060 (ν_{CN} in CN^-) and 370, 340 cm^{-1} (ν_{Au-Cl}).

Kinetics. (a) Conductance Changes. The conductances of the solutions of $[Au(N{-}N)(CN)_2X]$ were measured with a CMD 83 conductance meter (Radiometer, Copenhagen) in a cell with a shiny platinum electrode that was thermostated at the reaction temperature. The conductance, initially zero, increased with time, and the change followed a first-order rate law. The rate constants, k_{obsd}, were obtained from a nonlinear regression of the function $\Lambda_t = \Lambda_\infty + (\Lambda_0 - \Lambda_\infty)\exp(-k_{obsd}t)$ (where Λ_0, Λ_t, and Λ_∞ are the conductances at time 0, time t, and time after 10 half-lives, respectively) using the Gauss–Newton algorithm. Subsequent conductance changes are very slow and do not interfere.

(b) Spectrophotometric Changes. Reactions were initiated by adding solid $[Au(L{-}L)(CN)_2X]$ to the solvent previously brought to the reaction temperature in the thermostated cell of a Varian-Cary 219 spectrophotometer. The spectrum was scanned periodically, and the rate constants were calculated by optimizing the three parameters A_0 (absorbance at $t = 0$), A_∞ (absorbance at the end of the reaction), and k_{obsd} (the required rate constant) to the equation $A_t = A_\infty - (A_\infty - A_0)\exp(-k_{obsd}t)$ relating the absorbance (A_t) vs. time data, by using a Gauss–Newton algorithm.

Infrared spectra were measured with a Perkin-Elmer 683 infrared spectrophotometer.

Nuclear magnetic resonance spectra were measured with a Varian FT-80A NMR spectrometer using $[^2H_7]$dimethylformamide as solvent. δ is given as ppm from *H*-CO-N.

Results

(A) Nature of the 5-Coordinate Species in the Solid State and in Solution. The complex $[Au(phen)(CN)_2Br]$ prepared by the rapid reaction between 1,10-phenanthroline and the *trans*-$[Au(CN)_2Br_2]^-$ anion has been shown, in the solid state, to be a monomeric species with the gold 5-coordinate, the chelate spanning the apical and basal sites of a square pyramid, and the cyanide ligands trans in the basal plane.[11] The apical Au–N distance (2.608 Å) is considerably longer than the one in the basal plane (2.091 Å), and the N–Au–N angle (72°) is much less than that required for the square pyramid (90°). It has been assumed, on the basis of the similarity of properties, that the other $[Au(N{-}N)(CN)_2X]$ complexes studied in this paper (N–N = 1,10-phenanthroline, 5-methyl-1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline; X = Cl, Br) have similar structures.

The electrical conductance of a freshly prepared solution of any of these complexes in dimethylformamide, dimethyl sulfoxide, methanol, and butanone is that of a nonelectrolyte but increases with time in a first-order fashion.

The ^1H NMR spectrum of $[Au(phen)(CN)_2Br]$ in $[^2H_7]$dimethylformamide is recorded in Figure 1a. The simplicity of the spectrum (the assignments are listed in the figure) indicates that the halves of the phenanthroline are equivalent on the ^1H NMR time scale. The sharp singlet at δ 0.44, assigned to the 5- and 6-protons, is most diagnostic. Although the possibility that the geometry in solution differs from that in the solid state (a trigonal-bipyramidal molecule with the cyanide ligands in the axial positions) is worth considering, it is our view that the molecule is fluxional, the interconversion taking place by way of the trigonal-bipyramidal transition state. This behavior seems to be typical of such 5-coordinate species when a chelate spans basal and apical sites, e.g. *cis*-$[PtCl(PR_3)_2(N{-}N)]^+$ [14,15] and $[Pt(phen)_2CN]^+$.[16]

The ^1H NMR spectrum of the corresponding 5-methyl-1,10-phenanthroline complex has a sharp singlet signal for the methyl protons, which indicates the absence (on the NMR time scale) of two distinct isomers and which would be expected if this system also were fluxional.

(B) Nature of the Reaction Products in Solution. At the end of the reaction the final molar conductance (assuming one Au atom per "molecule") is approximatively half of that expected for a 1:1 electrolyte. This is true in all solvents studied and is independent of the concentration of the starting material. Consequently a simple equilibrium of the type

$$[Au(phen)(CN)_2X] \rightleftarrows [Au(phen)(CN)_2]^+ + X^-$$

can be ruled out. The change in conductance with time follows a first-rate law, and the kinetics will be discussed below. The change in conductance is paralleled by a change in absorbance, following the same first-order rate law, and it must be assumed that the two changes relate to the same process.

The final conductance can be readily explained if the redistribution reaction, observed by Harris,[9,10] when the trihalide 5-coordinate complexes, $[Au(N{-}N)X_3]$, are dissolved in nitrobenzene, nitromethane, or acetone, occurs, also in these cases, but much more slowly.

$$2[Au(N{-}N)(CN)_2X] \rightarrow [Au(N{-}N)(CN)_2]^+ + [Au(CN)_2X_2]^- + N{-}N$$

The data for the ^1H NMR spectrum of the 5-coordinate $[Au(phen)(CN)_2Br]$ complex (Figure 1a) were collected 8 min after mixing ($t_{1/2}$ = 30 min under the conditions used), and the signals at E, F, G, and H, which grow with time (Figure 1b–d), do so at the expense of those of the 5-coordinate substrate. After 120 min ($4t_{1/2}$) (Figure 1e), peak C has disappeared and the spectrum is almost identical with that of a freshly prepared equimolar solution of $[Au(phen)(CN)_2]^+$ and phen (Figure 1h). There appear to be significant loss of resolution and a minor shifting of peaks compared to those of the spectra of $[Au(phen)(CN)_2]ClO_4$ (Figure 1f) and phenanthroline (Figure 1g) measured separately, and further significant changes can be observed if the solutions are aged. The possibility that exchange between $[Au(phen)(CN)_2]^+$ and phen can account for the broadening is being investigated and will be reported elsewhere. The ^1H NMR spectra can give no information about the presence

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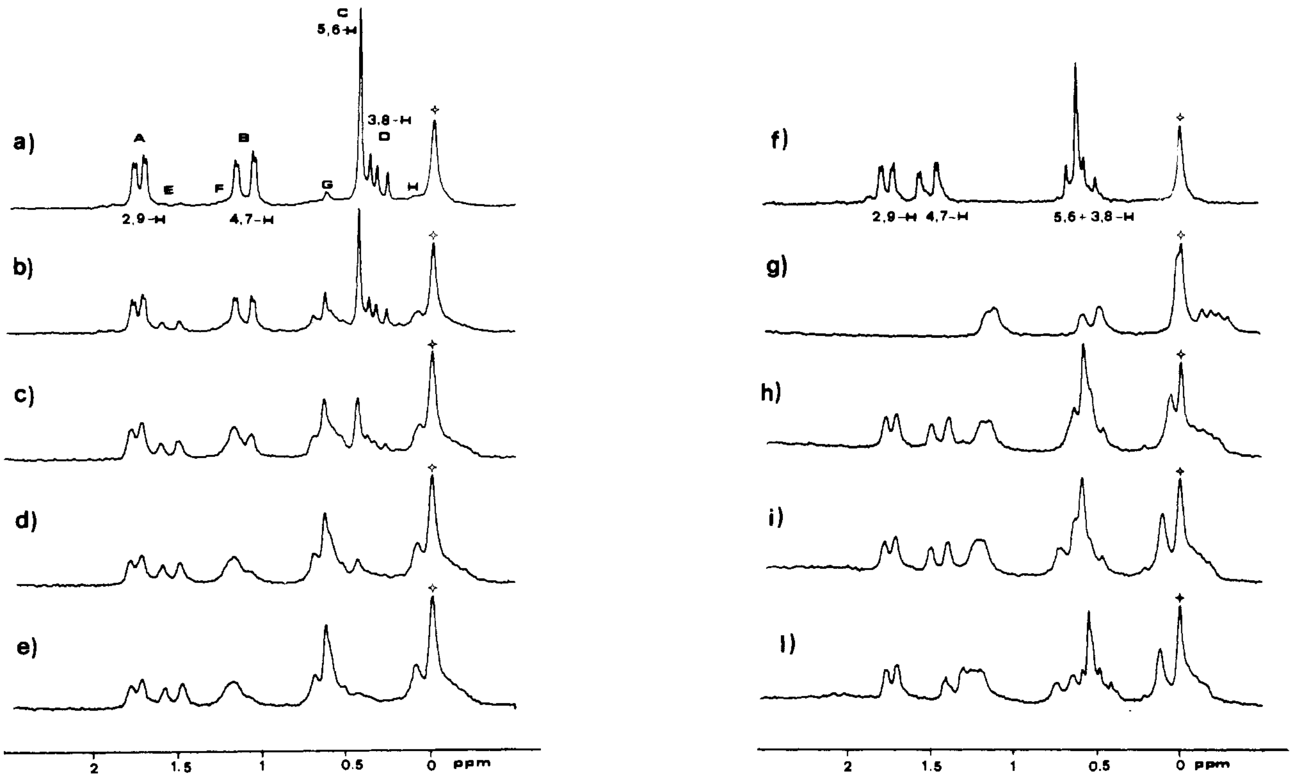

Figure 1. ^1H NMR spectra ([$^2H_7$]DMF, 35 °C): (a–e) [Au(phen)$(CN)_2$Br] (4 × 10^{-2} mol dm^{-3}) measured at various times after mixing [(a) 8 min, (b) 30 min, (c) 55 min, (d) 96 min, (e) 120 min]; (f) [Au(phen)$(CN)_2$]ClO_4 (2 × 10^{-2} mol dm^{-3}); (g) 1,10-phenanthroline (2 × 10^{-2} mol dm^{-3}); (h) equimolar (2 × 10^{-2} mol dm^{-3}) [Au(phen)$(CN)_2$]ClO_4 and 1,10-phenanthroline; (i) solution as in (h) after 60 min; (l) solution as in (i) to which was added an equimolar amount of *trans*-K[Au$(CN)_2Br_2$].

Table I. Products Isolated from Aged Solutions of [Au(phen)$(CN)_2$Br] or [Au(phen)$(CN)_2$Cl] in Dimethylformamide

procedure	% Au recovered	nature of solid product	color	how identified	conductance[a]/ Ω^{-1} mol^{-1} cm^2
aged soln + [$AsPh_4$]NO_3 + H_2O filtrate + aq $LiClO_4$	50	[$AsPh_4$][*trans*-Au$(CN)_2Br_2$]	yellow	*b*	
	50	[Au(phen)$(CN)_2$]ClO_4	yellow	*b,c*	67
aged soln + aq $LiClO_4$	100	[Au(phen)$(CN)_2$]ClO_4	yellow	*b,c*	67
water added to heated aged soln; cool to 0 °C	100	82% [Au(phen)$(CN)_2$Br] "product A"	red	*c, d*	38
water added to cold aged soln	100	[Au(phen)$(CN)_2$Br] "compd B"	yellow-orange	*b, c*	33
[Au(phen)$(CN)_2$Cl] in DMF heated at 50 °C for 2 days; add Et_2O	100	[Au(phen)$(CN)_2$Cl]	yellow	*b, c*	27
		"compd C"			
heat methanolic soln of chloro complex under reflux		"compd C"	yellow	*b, c*	27

[a] In DMF at 25 °C. [b] Infrared spectroscopy. [c] Elemental analysis. [d] Single-crystal X-ray diffraction.

of the [Au$(CN)_2Br_2$]$^-$ ion, nor indeed whether it is the cis or trans isomer.

The absorption spectrum in methanol at 35 °C of a mixture of [Au(phen)$(CN)_2$]ClO_4 (1.25 × 10^{-5} mol dm^{-3}), *trans*-K[Au$(CN)_2Br_2$] (1.25 × 10^{-5} mol dm^{-3}), and 1,10-phenanthroline (1.25 × 10^{-5} mol dm^{-3}) aged for 2 h is the same as that of a solution of the 5-coordinated species [Au(phen)$(CN)_2$Br] (2.5 × 10^{-5} mol dm^{-3}) that has been allowed to age for the same time. Spectrophotometric analysis does not allow us to say that the *cis*-[Au$(CN)_2Br_2$]$^-$ anion is absent, but that complex had not yet been prepared and it is not possible to say whether the spectra of the two isomers would be ambiguously similar. Inadequate solubility has so far prevented a meaningful study of the ^{13}C NMR spectra.

(C) Nature of the Materials Isolated from the Equilibrated Solution. Attempts to characterize the reaction products by isolating crystalline substances from the aged solutions have led to the identification of some interesting materials, and the results are summarized in Table I.

Addition of solid [$AsPh_4$]NO_3 to an aged solution of [Au(phen)$(CN)_2$Br] in DMF, followed by the addition of an equal volume of water, leads to the rapid precipitation of half of the gold present as *trans*-[$AsPh_4$][Au$(CN)_2Br_2$], the rest of the gold being precipitated as [Au(phen)$(CN)_2$]ClO_4 when aqueous $LiClO_4$ is added to the filtrate. However, if the aqueous $LiClO_4$ is added first, *all* of the gold is precipitated as [Au(phen)$(CN)_2$]ClO_4.

The materials precipitated when water is added to an aged DMF solution depend upon the precise condition used. Product A analyses as a mixture of 82% [Au(phen)$(CN)_2$Br] and 18% [Au(phen)(CN)Br_2], and an X-ray diffraction analysis of a single crystal of this red material, which will be published elsewhere,[17] shows a 5-coordinate, square-pyramidal Au(III) with Au(phen)$(CN)_2$ planes stacking with unsymmetrical Br–Au···Br–Au··· perpendicular to them. The diffraction data indicate an isomorphous replacement of about 8% of the CN ligands by Br.

The yellow-orange crystals of compound B, which are obtained by rapid precipitation from a cold aged solution of [Au(phen)$(CN)_2$Br], were unsuitable for X-ray analysis, and any attempt at recrystallization yielded product A. B is an isomer of the 5-coordinate nonelectrolyte starting material but differs from it in that freshly prepared solution in DMF has a conductance of 33–38 Ω^{-1} mol^{-1} cm^2 at 25 °C and does not change significantly

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(17) Gilli, G., private communication, 1986.

Table II. First-Order Rate Constants for Reactions of [Au(N-N)(CN)$_2$X] Substrates[a]

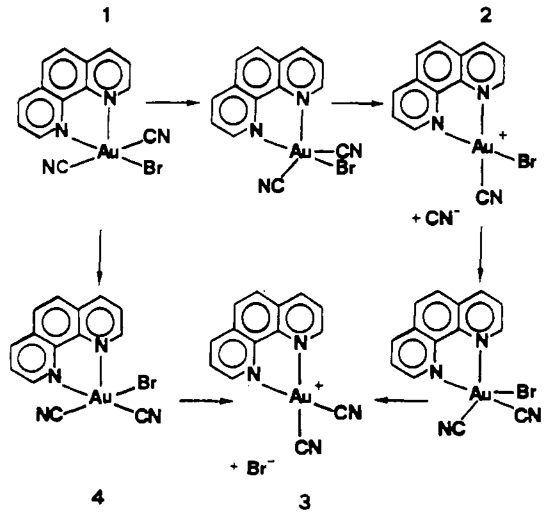
N-N	X	10^3 × [substrate]/ mol dm^{-3}	solvent	T/ °C	10^3k_{obsd}/s^{-1} [e]
1,10-phen	Cl	2.00	DMF	25	0.181 ± 0.004
1,10-phen	Cl	2.00	DMF	30	0.307 ± 0.003
1,10-phen	Cl	2.00	DMF	35	0.531 ± 0.007
1,10-phen	Cl	2.00	DMF	40	0.836 ± 0.008
1,10-phen	Cl	*b*	DMF	40	0.88 ± 0.05[c]
1,10-phen	Cl	2.00	DMF	45	1.51 ± 0.02
1,10-phen	Br	2.00	DMF	24.5	0.138 ± 0.005
1,10-phen	Br	2.00	DMF	30	0.252 ± 0.007
1,10-phen	Br	2.00	DMF	35	0.412 ± 0.002
1,10-phen	Br	*b*	DMF	35	0.419 ± 0.025[c]
1,10-phen	Br	2.00	DMF	40	0.663 ± 0.002
1,10-phen	Br	*b*	DMF	40	0.7 ± 0.2[c]
1,10-phen	Br	2.00	DMF	45	1.109 ± 0.006
5-Me-1,10-phen	Br	2.00	DMF	25	0.202 ± 0.002
5-Me-1,10-phen	Br	2.00	DMF	30	0.330 ± 0.008
5-Me-1,10-phen	Br	2.00	DMF	35	0.63 ± 0.01
5-Me-1,10-phen	Br	2.00	DMF	40	0.93 ± 0.01
5-Me-1,10-phen	Br	2.00	DMF	45	1.45 ± 0.01
5-Me-1,10-phen	Cl	2.00	DMF	25	0.232 ± 0.001
5-Me-1,10-phen	Cl	2.00	DMF	35	0.715 ± 0.005
5-Me-1,10-phen	Cl	2.00	DMF	45	1.93 ± 0.04
1,10-phen	Cl	2.00	DMF/H$_2$O (5%)[d]	45	2.49 ± 0.02
1,10-phen	Cl	2.00	DMF/H$_2$O (8%)	45	2.98 ± 0.02
1,10-phen	Cl	2.00	DMF/H$_2$O (11%)	45	3.58 ± 0.02
1,10-phen	Cl	0.495	DMF	35	0.52 ± 0.01
1,10-phen	Cl	1.00	DMF	35	0.51 ± 0.01
1,10-phen	Cl	2.00	DMF	35	0.50 ± 0.01
1,10-phen	Cl	3.68	DMF	35	0.51 ± 0.01
1,10-phen	Br	2.00	Me$_2$SO	20	1.88 ± 0.07
1,10-phen	Br	2.00	Me$_2$SO	25	3.2 ± 0.1
1,10-phen	Br	2.00	Me$_2$SO	35	8.2 ± 0.2
1,10-phen	Cl	2.00	Me$_2$SO	20	1.2 ± 0.1
1,10-phen	Cl	2.00	Me$_2$SO	30	2.5 ± 0.1
1,10-phen	Cl	2.00	Me$_2$SO	40	5.5 ± 0.2
1,10-phen	Br	2.00	butanone	30	0.146 ± 0.007
1,10-phen	Br	2.00	butanone	40.2	0.352 ± 0.006
1,10-phen	Br	2.00	butanone	50	0.82 ± 0.01
1,10-phen	Cl	2.00	butanone	40	0.71 ± 0.01
1,10-phen	Cl	*b*	ClCH$_2$CH$_2$Cl	32	0.247 ± 0.005[c]

[a] Determined from conductance changes except where otherwise indicated. [b] Complex concentration less than 10^{-4} mol dm^{-3}. [c] Determined spectrophotometrically. [d] Water content in volume percent. [e] Uncertainties on the observed rate constants were calculated as the *i* element in the diagonal of the inverse matrix relative to the nonlinear regression (using the Gauss–Newton algorithm) and are reported with no confidence interval.

with time. This is approximately half the conductance expected for a 1:1 electrolyte (60–70 Ω^{-1} mol^{-1} cm^2). A similar species (compound C) can be obtained from the analogous chloro complex. A detailed description of these and other materials that can be isolated and characterized will be published elsewhere.

(D) Kinetics of the Reaction. The increase in conductance with time follows a first-order rate law, and the rate constants, k_{obsd}, for the various substrates in a range of solvents at different temperatures, are collected in Table II. The UV absorbance also changes with time in a first-order fashion, and values for k_{obsd} are also collected in Table II. The spectrophotometric and conductometric rate constants agree within experimental error. The changes in the ^{1}H NMR spectra also follow the same first-order rate law, but because of the large experimental error and the large amounts of material required, no systematic quantitative studies were carried out.

Scheme I



Discussion

[Au(phen)(CN)$_2$Br], shown to be 5-coordinate and monomeric in the solid state, dissolves in a variety of solvents to give, initially, a 5-coordinate, monomeric, nonelectrolyte species. The ^{1}H NMR spectrum is inconsistent with the unsymmetrical structure of the solid state, where the two Au–N bonds are of very different length, and a fluxional behavior is indicated. The subsequent reaction leads to an increase of conductance to a point where it is half of that expected from a 1:1 electrolyte caused by the loss of an anionic ligand. Studies of the solution at the end of the reaction indicate that there has been a redistribution of the sort that has been observed much more rapidly for the [Au(phen)X$_3$] species[9,10]

$$2[\mathrm{Au(N{-}N)(CN)_2X}] \rightarrow [\mathrm{Au(N{-}N)(CN)_2}]^+ + trans\text{-}[\mathrm{Au(CN)_2X_2}]^- + \mathrm{N{-}N}$$

Apart from the solvolysis of the [Au(N-N)(CN)$_2$]$^+$ cation, which causes considerable interference in protonic solvents such as methanol, the reaction occurs in a single first-order stage, and the k_{obsd} is independent of the starting concentration of substrate.

It has already been pointed out that, whether or not one agrees to call species like [Au(phen)(CN)$_2$Br], *cis*-[Pt(phen)(PR$_3$)$_2$Cl]$^+$,[14,15] or [Pt(phen)$_2$CN]$^+$ [16] 5-coordinate, the fluxionality of the bidentate ligand arises from a facile exchange of the short-bonded N and the long-bonded N. The species can therefore be looked upon as lying part of the way along the reaction coordinate for the substitution of N by N. In principle, it can also represent a stage in the replacement of one of the anionic ligands by the incoming N leading to the formation of the chelate. However, in the absence of any rearrangement, the only ligands suitably placed to act as leaving group are the tightly bound cyanides. It is conceivable that the slowness of the ionization of the 5-coordinate species (**1**) (Scheme I), leading to the [Au-

Table III. Activation Parameters for Reactions of Substrates in Different Solvents

N-N	X	solvent	10^3k_{obsd}/s^{-1} [a]	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/cal K^{-1} mol^{-1}
1,10-phen	Br	DMF (36.7)[b]	0.146	18 ± 1	−14 ± 3
1,10-phen	Cl	DMF	0.178	19.8 ± 0.8	−9 ± 3
5-Me-1,10-phen	Br	DMF (36.7)[b]	0.205	18 ± 1	−16 ± 0.3
5-Me-1,10-phen	Cl	DMF	0.234	19.0 ± 0.4	−11 ± 1
1,10-phen	Br	Me$_2$SO (48.9)[c]	3.20	16.6 ± 0.1	−14.0 ± 0.1
1,10-phen	Cl	Me$_2$SO	1.76	13.5 ± 0.2	−25.5 ± 0.8
1,10-phen	Br	butanone (18.4)[c]	0.098	16.1 ± 0.2	−22.7 ± 0.6

[a] Interpolated at 25 °C from best linear fit of ln (k_{obsd}/T) vs. T^{-1} plots. [b] Dielectric constant at 25 °C.[23] The value for *sym*-dichloroethane is 10.4.[23] [c] Dielectric constant at 20 °C.[23]

(phen)(CN)Br]$^+$ intermediate (**2**), is due to this, the trihalo complexes undergoing this change rapidly. However, the subsequent behavior can be accounted for only if the released CN$^-$ displaces Br$^-$ from **2** before it leaves its environment, with formation of [Au(phen)(CN)$_2$]$^+$ (**3**). The isolation of some [Au(phen)(CN)Br]$^+$ is not inconsistent with this mechanism, but in view of the lability of the reaction products, it is not compelling evidence. Alternatively, the rate-determining step might be an intramolecular rearrangement of **1** that allows CN and Br to exchange sites (**4**), which is followed rapidly by loss of Br$^-$ in a classic fashion to give **3**.

A very rapid reaction between the released Br$^-$ and the unreacted 5-coordinate substrate will lead to the formation of *trans*-[Au(CN)$_2$Br$_2$]$^-$ and free phenanthroline by a normal substitution pathway that is the reverse of the entry of the first nitrogen of the chelate. As a result, only half of the substrate is converted to [Au(phen)(CN)$_2$]$^+$ while the rest goes to *trans*-[Au(CN)$_2$Br$_2$]$^-$. The very rapid reaction between [Au(phen)(CN)$_2$Br] and Br$^-$ in DMF to give *trans*-[Au(CN)$_2$Br$_2$]$^-$ has been examined qualitatively and shown to be complete before the first spectrum could be measured. [Au(phen)(CN)$_2$]$^+$ also reacts rapidly with Br$^-$ (as might be expected from the strong trans effect of cyanide), but the product appears to be the trans isomer as well. These reactions are now being studied in detail.

The rate constants at a common temperature and the activation parameters are collected in Table III. The rate constants appear to be markedly dependent upon the nature of the solvent, the reaction in Me$_2$SO being significantly faster than that in DMF, which in turn is faster than the reactions in butanone and *sym*-dichloroethane. The reaction could not be studied in water, but addition of water to DMF leads to a large increase in reactivity. A plot of k_{obsd} against percent by volume of water is almost linear and extrapolates smoothly to the value measured in pure DMF. The general tendency for the rate constant to parallel the dielectric constant of the medium suggests that there is charge separation on going to the transition state of the rate-determining step and thus favors the successive displacement mechanism. However, one should bear in mind that this type of reasoning may lead to false conclusions as it did in the case of the PR$_3$-catalyzed cis-trans isomerization of [Pt(PR$_3$)$_2$Cl$_2$], where an ionization mechanism has been demonstrated[18] even though the rate is much retarded in polar solvents.[19]

The difference in the reactivities of 1,10-phenanthroline and 5-methyl-1,10-phenanthroline complexes is too small to be considered significant, but the 5-coordinate complex of 2,9-dimethyl-1,10-phenanthroline reacts very slowly indeed ($t_{1/2} > 100$ h at 50 °C in DMF). This is to be expected since the methyl substituents offer a considerable increase in steric hindrance on going to any trigonal-bipyramidal transition state for substitution (for the same reason that orthomethylation in the cis ligands, R, decreases the substitutional lability of *cis*-[Pt(PEt$_3$)$_2$RCl][20,21]). There will also be strong hindrance between the methyl groups and the adjacent ligands in the square-planar chelated product.

The difference in the reactivities of the chloro and bromo complexes is small, and either may be the more reactive species. Such a similarity is not uncommon in square-planar substitution when these ligands are leaving groups or are cis to them.[22]

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Registry No. **1**, 105250-54-2; **3**·ClO$_4$, 108189-79-3; [Au(5-Mephen)(CN)$_2$Br], 108189-74-8; [Au(phen)(CN)$_2$Cl], 108189-75-9; [Au(5-Mephen)(CN)$_2$Cl], 108189-76-0; [Au(2,9-Me$_2$phen)(CN)$_2$Cl], 108212-07-3; [Au(2,9-Me$_2$phen)(CN)$_2$Br], 108189-77-1; *trans*-K[Au(CN)$_2$Br$_2$], 30643-42-6; *trans*-K[Au(CN)$_2$Cl$_2$], 30643-41-5; [AsPh$_4$][*trans*-Au(CN)$_2$Br$_2$], 108189-80-6; [Au(phen)(CN)(Br)$_2$], 108189-81-7.

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Deprotonation of the α-Carbon in Amino Acid Amides and Peptides Chelated to Ruthenium(III)

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Deprotonations of chelates of NH$_2$CH$_2$CONR^{1}R^2 N,O-bound to Ru(III) (R^1 = H, R^2 = H, C$_2$H$_5$, CH$_2$COO$^-$; R^1 = CH$_3$, R^2 = CH$_2$COO$^-$) after they were mixed with buffer solutions (pH 6.3–8.5) were followed spectrophotometrically and electrochemically: $k = 0.055 \pm 0.004$ s^{-1} (R$_1$ = R$_2$ = H); $k = 0.057 \pm 0.004$ s^{-1} (R$_1$ = H, R$_2$ = CH$_2$COO$^-$); $k = 0.032 \pm 0.002$ s^{-1} (R$_1$ = CH$_3$, R$_2$ = CH$_2$COO$^-$); $\mu = 0.1$ M, 23 ± 2 °C. The chelate of glycylsarcosine (R$_1$ = CH$_3$, R$_2$ = CH$_2$COO$^-$) was prepared for the first time and showed a pK_a = 6.5 ± 0.1, similar to pK_a's observed before for similar chelates. It is suggested that the site of deprotonation is the chelate ring methylene group, and not the dangling amido group as suggested before. Extra stabilization of the deprotonated species is ascribed to π interaction that involves the half-filled t$_{2g}$ orbital of Ru(III) and p orbitals of the two sp^2-hybridized carbon atoms and the oxygen atom. This is consistent with NMR results in which full exchange of the methylene protons with deuterium is observed at neutral pH within a few minutes. The deprotonation process is thought to be slow because of a configuration change of the chelate ring from a nonplanar strain-free configuration to a planar strained configuration of the enolate anion produced.

Introduction

Ruthenium-modified proteins have been used to study electron transfer between ruthenium ions and metal centers of metalloproteins.[1-3] The ruthenium moiety has also been attached to several proteins as a probe of various effects on the structure of proteins.[4] We have been studying the interaction between am-

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