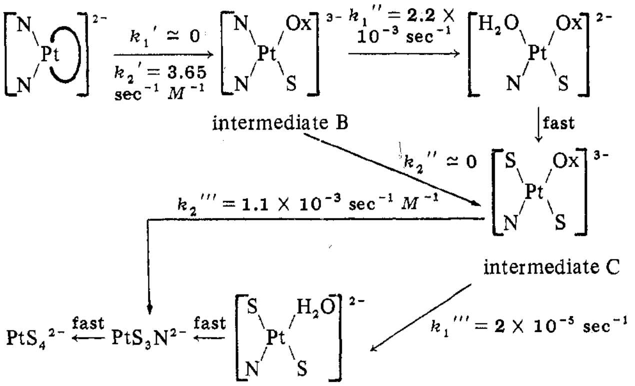
Scheme I



N = NO_2; S = SCN; Ox = monodentate C_2O_4; ◯ = bidentate C_2O_4

next case, the hypothesis under examination was that of a stabilization of the activated complex due to the formation of a hydrogen bridge between the entering H_2O molecule and the "free" end of the unidentate oxalato. This reaction mechanism is similar to that proposed for some substitution reactions of octahedral amino complexes and has been named S$_N$2FS[15] (where the entering water molecule is hydrogen bonded both to a leaving group and to an inert amine group) or to the "anchoring effect", invoked to explain the kinetic behavior of the bidentate amine as entering groups in Pt(II) complexes.[16]

For the third step of the reaction, where $k_1''' \ll k_2'''$[SCN], two mechanisms are possible: (1) the oxalato ligand substitution precedes NO_2 (eq 1); (2) the NO_2 ligand is the first group to leave, followed by C_2O_4 in an even faster reaction. The second mechanism is less probable, because, in the presence of the unidentate oxalato ligand, it should lead to the same kinetic results of the second step, i.e., $k_1''' > k_2'''$[SCN]. On the contrary in mechanism (1) the entropy values also appear to support the mechanism proposed in Scheme I. In the third step $\Delta S^‡$ is higher than in the first, despite the increased charges of the anion reagents. This result is in agreement with that of the $Pt(C_2O_4)_2^{2-} + SCN^-$,[1] where the opening process of the bidentate ring (first step) has a much more negative $\Delta S^‡$ than that of the substitution reaction of the unidentate oxalato group (second step).

In Table II the kinetic salt effect of the Ba^{2+} ion is also reported, confirming the results obtained in other Pt(II) reactions.[1,2,17] The specific character of these results can be explained by two different mechanisms. In the first, similar to that postulated for the electrophilic catalysis, the cations interact with the Pt(II) anions, through the elongated z axis.[18] By removing d valence orbital electrons, the metal can then more readily accept the bonding electrons from the entering nucleophile. Another explanation is that the cation electrophilic attack takes place on the coordinated oxalato group, causing in this case Pt–O bond rupture.[1] It is probable that both mechanisms are present, because on the substitution reaction of Pt(II) complexes the bond-making and the bond-breaking processes are equally important.

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Registry No. $Pt(NO_2)_2C_2O_4^{2-}$, 54516-14-2; *cis*-$[Pt(NH_3)_4]_3[PtOx(NO_2)_2SCN]_2$, 54531-59-8; *trans*-$[Pt(NH_3)_4]_3[PtOx(SCN)_2NO_2]_2$, 54531-61-2; SCN^-, 302-04-5; $C_2O_4^{2-}$, 338-70-5; NO_2^-, 14797-65-0.

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Notes

Contribution from the Istituto di Chimica Generale ed
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Five-Coordinate Copper(II) Complexes. Synthesis and Properties of $[Cu(tren)L]^{2+}$ Cations

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The presence in solution of five-coordinate copper(II) complexes of the type $[Cu(tren)X]^{n+}$ (n = 1 or 2; tren = 2,2',2''-triaminotriethylamine) has been previously suggested.[2] However, such complexes have not been isolated except in the case of [Cu(tren)NCS]SCN.[3] A trigonal-bipyramidal structure has been deduced for the latter complex from X-ray diffraction studies.[4]

We now report the synthesis and characterization of some complexes of the type $[Cu(tren)L]Y_2$ (L = amine ligand; Y^- = BPh_4^- or ClO_4^-) (Table I), prepared by two different general procedures. By the first method (A) the complexes have been obtained by the reaction (at room temperature in 2% $NaHCO_3$ aqueous solution) of equimolar ratios of a copper(II) salt (sulfate or chloride) and the tetradentate and the monodentate amine ligands. The immediate color change of the solution from light to very deep blue indicated that a very fast reaction had taken place. The products were easily precipitated from the solution by adding $NaBPh_4$. By the second method (B)

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Table I. Properties of Some Five-Coordinate Copper(II) Complexes

Compd	Mp,[a] °C	Molar conductivities,[b] cm² ohm⁻¹ *M*⁻¹	λ_{max}, cm⁻¹ (λ shoulder)	% C		% H		% N	
				Calcd	Found	Calcd	Found	Calcd	Found
[Cu(tren)OH]BPh_4	159 dec	54.0	12,100 (14,300)	66.0	66.9	7.15	7.15	10.3	10.5
[Cu(tren)OH]$ClO_4 \cdot 2H_2O$[c]	262 dec	69.2	12,100 (12,300)	19.9	19.8	6.3	6.3	15.5	15.7
[Cu(tren)py]$(BPh_4)_2$	108 dec	111.2	12,500 (14,890)	76.5	75.8	6.8	7.1	7.6	7.6
[Cu(tren)NH_2Ph]$(BPh_4)_2$	110 dec	109.0	12,300 (14,800)	76.6	76.5	6.9	7.0	7.4	7.3
[Cu(tren)-4-$CH_3O(NH_2Ph)$]$(BPh_4)_2$	112 dec	107.5	12,600 (15,160)	75.4	74.3	6.9	7.1	7.2	7.3
[Cu(tren)NCS]BPh_4	148 dec	55.3	11,900 (14,300)	63.4	62.5	6.5	6.6	11.9	11.7
[Cu(tren)NH_3]$(BPh_4)_2$	124 dec	119.0	12,540 (14,900)	75.0	74.2	7.1	6.9	8.1	8.2

[a] Melting points were determined in capillaries and are uncorrected. [b] Molar conductivities were determined in 10^{-3} *M* nitroethane solutions at 25°. [c] Percent Cl: calcd, 9.8; found, 10.3.

the complexes have been obtained by reaction in acetone at room temperature of an equimolar ratio of the monodentate amine ligand with the complex [Cu(tren)OH]BPh_4. Spectrophotometric analysis of the solution indicates that the substitution of the hydroxyl group by the amine nucleophile is very fast and readily accomplished in a polar aprotic solvent. Since the presence in aqueous solution of the equilibrium (eq 1, pK_a = 9.2)

$$[Cu(tren)H_2O]^{2+} + H_2O \rightleftharpoons [Cu(tren)OH]^+ + H_3O^+ \qquad (1)$$

has been previously demonstrated,[2] it seems reasonable to suppose that the aquo complex [Cu(tren)H_2O]$^{2+}$ is the intermediate in which substitution of the solvent molecule by the monodentate amine ligand takes place. The complexes have been characterized by elemental analysis, magnetism, conductivities, and ir spectra. Even though the magnetic moments (determined by the Evans method[5]) which fall in the range 1.9–2.2 BM are not good indicators of geometrical structure, they do indicate a 2+ oxidation state for the metal atom and allow us to exclude metal–metal interaction, supporting a monomeric structural formulation for the compounds at room temperature. The molar conductivities of 10^{-3} *M* solutions in nitroethane at 25° (Table I) are in the range 50–70 cm² ohm⁻¹ *M*⁻¹ for the complexes of the type [Cu(tren)L]Y (L = NCS or OH) and suggest that they are 1:1 electrolytes and that the differences are due to the different ionic mobilities of noncoordinated counteranions. For the complexes in which L is a neutral ligand, conductivities characteristic of 1:2 electrolytes are found.

Ir spectra on solid samples show common absorptions characteristic of the tetradentate amine ligand, of the L ligand, and of the noncoordinated group.

It has recently been found by X-ray analysis that the complexes [Cu(en)$_2$](SCN)$_2$,[6] [Cu(tren)NCS]SCN,[7] and [Cu(trien)SCN]SCN[8] (en = $NH_2(CH_2)_2NH_2$; trien = $NH_2(CH_2)_2(NH(CH_2)_2)_2NH_2$) have different structures. The first exhibits a square-planar geometry in which the four nitrogen donor atoms are coplanar with the metal atom. The two thiocyanate groups are on opposite sites of the plane at nonbonded distances from the copper atom (the smaller Cu–S distance is 3.27 Å). The second derivative has a trigonal-bipyramidal structure with the tren behaving as a tripod-like ligand and only one thiocyanato group bonded through the nitrogen to the metal atom in an apical position. The structure of the third compound is a square pyramid with one NCS ligand bonded through the sulfur in the apical position (the Cu–S bond length is 2.61 Å). While the [Cu(tren)NCS]$^+$ cation shows the same electronic spectrum in the solid state and in solution, the other two complexes behave differently; i.e., their solution spectra differ from the spectra of the solids.[9] This indicates that the molecular structures of [Cu(en)$_2$](NCS)$_2$ and [Cu(trien)(SCN)]SCN complexes change upon dissolution. The unique behavior of the [Cu(tren)NCS]$^+$ compound has been rationalized by taking into account the fact that in a trigonal-bipyramidal structure positions are not available for coordination of solvent molecules and therefore in this case the molecular geometry seems to be the same in solid and in solution. For all the complexes here reported, good agreement between solution and solid electronic spectra have been found (Table I). Generally the spectra show an absorption in the 12,000–12,600-cm⁻¹ region ($\epsilon_{max} \simeq 130$ cm⁻¹ *M*⁻¹) and a shoulder at 14,300–15,400 cm⁻¹. Occasional shifts (100 cm⁻¹) in λ_{max} can reasonably be attributed to solvation effects rather than to changes in molecular geometry (which should lead to large differences of ~4000–5000 cm⁻¹).

Experimental Section

Materials. Commercial reagent grade chemicals were used without further purification. 2,2',2''-Triaminotriethylamine was prepared according to published methods.[10,11] The complex [Cu(tren)NCS]SCN was obtained following the procedure reported elsewhere.[3]

Apparatus. Magnetic susceptibilities in solution were measured by the method of Evans.[5] Conductivities of about 10^{-3} *M* solutions of complexes in nitroethane at 25° were measured with an LKB bridge. Infrared spectra of KBr pellets or Nujol mulls were recorded on a Perkin-Elmer 621 spectrophotometer. Electronic spectra were recorded with a Beckman DK-2A recording spectrophotometer. Visible mull spectra were obtained from Nujol mulls supported on filter paper.

Syntheses of Complexes. The two general procedures by which the complexes of the type [Cu(tren)L]$(BPh_4)_2$ (L = Py, NH_2Ph, NH_2PhOCH_3) were obtained are the following. In the first method (A), $CuSO_4 \cdot 5H_2O$ (2.49 g, 10 mmol) and tren·3HCl (3.07 g, 12 mmol) were placed in water (50 ml). The pH of the solution was raised to 8 by slowly adding under magnetic stirring a 33% solution of NaOH (4.5 ml) and finally $NaHCO_3$ (1 g). To the resulting solution the appropriate amine (40 mmol) was then added and the color changed from light to deep blue. The light blue precipitate, formed by adding $NaBPh_4$ (6.84 g, 20 mmol) to the solution, was filtered, washed with water, and dried in a vacuum desiccator containing P_2O_5. The yield was in the 85–93% range. The [Cu(tren)OH]BPh_4 complex was obtained by the same method except that the $NaBPh_4$ was added to the solution of $CuSO_4 \cdot 5H_2O$ and tren·3HCl after raising the pH to 13 with 33% NaOH.

In the second method (B), to a slurry of [Cu(tren)OH]BPh_4 (0.545 g, 1 mmol) in acetone (15 ml) the appropriate amine (1.5 mmol) was added at room temperature, under magnetic stirring. Further addition of $NaBPh_4$ (0.342 g, 1 mmol) in 100 ml of water led to precipitation of the product, which was filtered, washed, and dried as described above; yield 80–87%.

$[Cu(tren)OH]ClO_4{\cdot}2H_2O$. A solution of tren·3HCl (1.2 g, 4.7 mmol) in water (50 ml) was treated with a 33% NaOH solution (1.6 ml) under vigorous magnetic stirring. The NaCl which resulted upon addition to the solution of absolute ethanol (90 ml) was filtered off. To the free tetradentate ligand solution was then added $CuCl_2{\cdot}2H_2O$ (0.767 g, 4.5 mmol) and $LiClO_4$ (0.48 g, 4.5 mmol). The dark blue solution was evaporated to a volume of about 25 ml and slowly cooled in a dewar to room temperature. The blue crystals thus obtained were filtered, washed with methanol and ether, and vacuum-dried; yield 54%.

$[Cu(tren)NCS]BPh$. This complex was obtained by passing a solution of [Cu(tren)NCS]SCN (0.65 g, 2 mmol) in water (30 ml) through a column of an anionic resin (Dowex 1-X4, 50–100 mesh) in ClO_4^- form. The addition of $NaBPh_4$ (0.68 g, 2 mmol) to the resulting blue solution afforded a precipitate, which was washed with H_2O and vacuum-dried over P_2O_5.

$[Cu(tren)NH_3](BPh_4)_2$. This compound was obtained by passing gaseous ammonia for 15 min through an acetone solution (30 ml) of the $[Cu(tren)OH]BPh_4$ derivative (1.09 g, 2 mmol). During this time a color change of the solution from deep green to dark blue was observed. The final product, obtained by adding an aqueous solution (100 ml) of $NaBPh_4$ (0.69 g, 2 mmol), was filtered, thoroughly washed with H_2O, and vacuum-dried; yield 85%.

Registry No. $[Cu(tren)OH]BPh_4$, 54750-19-5; $[Cu(tren)OH]ClO_4$, 54750-20-8; $[Cu(tren)py](BPh_4)_2$, 54689-08-6; $[Cu(tren)NH_2Ph](BPh_4)_2$, 54689-10-0; $[Cu(tren)\text{-}4\text{-}CH_3O(NH_2Ph)](BPh_4)_2$, 54689-12-2; $[Cu(tren)NCS]BPh_4$, 52665-52-8; $[Cu(tren)NH_3](BPh_4)_2$, 54689-14-4.

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Nuclear Magnetic Resonance Studies of the Solution Chemistry of Metal Complexes. XII. Binding of Methylmercury by Methionine[1]

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The complexation of metal ions by the amino acid methionine has been the subject of considerable research, with much of the interest focusing on participation of the thioether group in the metal binding.[2-7] Li and Manning showed by a comparison of the formation constants of the glycine and methionine complexes of Zn(II) that binding of Zn(II) by methionine is through the amino and carboxylate dentates.[2] In a similar but more extensive study, Lenz and Martell concurred with the conclusions of Li and Manning and proposed that, of the metal ions Ag(I), Ca(II), Cd(II), Co(II), Cu(II), Hg(II), Mg(II), Mn(II), Ni(II), Pb(II), and Sr(II), only Ag(I) binds to the thioether group.[3] McAuliffe, Quagliano, and Vallarino[4] showed by infrared spectroscopy that, in the solid state at least, binding of several of these and other metal ions by anionic methionine is as proposed by Lenz and Martell.[3] More recently, however, Natusch and Porter have demonstrated by proton magnetic resonance (PMR) spectroscopy that, in acidic solution, a previously undetected complex forms in which Hg(II) is bonded solely to the thioether group.[7,8]

The observation that the thioether group can bind Hg(II) in acidic solution suggests that this group might be an important binding site for methylmercury, whose importance in mercury poisoning is well established. In this paper, we present PMR results which show that one-coordinate methylmercury binds to the thioether group of methionine in acidic solution. Formation constants have been determined for this interaction and for the binding of methylmercury by the amino group, the exclusive binding site in basic solution. From these and previously reported results, binding sequences are derived as a function of pH for the binding of methylmercury by the sulfhydryl, amino, carboxyl, and thioether ligands.

Experimental Section

Methylmercuric hydroxide (Alfa Inorganics) was purified and a stock solution was prepared as described previously.[9] The stock solution was standardized by titration of aliquots with a standard sodium chloride solution in an acidified ethanolic medium; the end point was located potentiometrically by means of an Ag–AgCl indicating electrode.[1] Methionine (British Drug Houses) was used as received. Tetramethylammonium (TMA) nitrate was prepared by titration of a 25% aqueous solution of tetramethylammonium hydroxide (Eastman Organic Chemicals) with HNO_3 to a neutral pH.

pH measurements and PMR measurements were made as described previously.[1,9] Chemical shifts were measured relative to the central resonance of the TMA triplet or the *tert*-butyl resonance of *tert*-butyl alcohol but are reported relative to the methyl resonance of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS). Positive shifts correspond to resonances of protons less shielded than those of DSS.

Solutions were prepared by the procedures described previously.[1,9] The pH was adjusted with HNO_3 or KOH. The nitrate anion forms a complex with methylmercury,[10] but the interaction is so weak[11] that it does not compete with hydroxide or methionine for the methylmercury cation.

Results and Discussion

The chemical shifts of the methyl and methine protons of methionine, which give rise to a singlet and a triplet, are shown as a function of pH in Figure 1 for a solution containing 0.150 M methionine and for a solution containing 0.160 M methionine and 0.160 M methylmercury. At pH <2, the chemical shift of the methine proton is not affected by the presence of methylmercury, whereas the methyl protons are deshielded, indicating that, in this pH range, the thioether group is the binding site. As the pH is increased from pH 2, the two chemical shift curves for the methine proton become increasingly different, while those for the methyl protons approach each other, indicating that the methylmercury is shifting from the thioether group to the other end of the molecule. At pH ~8–9, coordination is exclusively to the amino end. As the pH is increased above pH 8–9, the complex begins to dissociate, as indicated by the shift of the methine resonance of the methylmercury-containing solution toward that of free methionine. The overlap of the two curves at pH >13.5 indicates complete dissociation at this pH.

The chemical shift and the mercury–proton spin–spin coupling constant of the methyl protons of methylmercury also indicate complexation of methylmercury by methionine. In Figure 2, the coupling constant is shown as a function of pH for a solution containing 0.190 M methylmercury and for a solution containing 0.160 M methionine and 0.160 M methylmercury. The pH dependence of the coupling constant of the 0.190 M methylmercury solution is due to the formation of $(CH_3Hg)_2OH^+$, a very small amount of $(CH_3Hg)_3O^+$, and