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A Copper(I) *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine Complex and Its Carbon Monoxide Adduct in Aqueous Solutions

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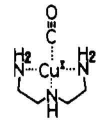
Copper(I) ion forms a stable 1:1 complex with pmdien (2,5,8-trimethyl-2,5,8-triazanonane, **7**) in CO-saturated or CH_3CN-containing *aqueous* solutions, due to the formation of a stable 1:1 CO or CH_3CN adduct. The formation constants of [Cu(pmdien)(CO)]$^+$ (**8**) and [Cu(pmdien)($NCCH_3$)]$^+$ have been established by the pH-metric titration and polarographic methods. Moreover, crystalline [Cu(pmdien)(CO)]ClO_4 has been isolated from CO-saturated *aqueous* solution. The observed ν_{CO} bands of the CO adduct **8** at 2082 cm^{-1} (KBr pellet) and 2088 cm^{-1} (aqueous solution) agree with the end-on CO coordination.

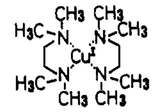
There is a growing interest in the chemistry of Cu^I complexes in solution. This interest stems from the role of Cu^I in biological systems,[1] in the separation of CO or C_2H_4,[2] in catalysis, in free-radical reactions, and in other essential redox processes. Though some of these processes involving Cu^I occur in aqueous solutions, there are few synthetic ligands (e.g. cimetidine)[3] that stabilize Cu^I in aqueous media. Of the common nitrogen donor ligands only those including unsaturated amines can form stable Cu^I complexes in aqueous solutions.[1,4] However, these ligands themselves are often redox active due to their unsaturation and therefore may not be suitable in studies of catalytic systems.

Recent studies indicate that a variety of Cu^I complexes with saturated aliphatic amines can be formed in *organic* solvents, e.g. MeOH and Me_2SO, in the presence of CO or olefin.[2,5-10] Such Cu^I complexes (e.g. [Cu(dien)(CO)]$^+$ (**1**))[5] have often been isolated for X-ray structure analysis, where dien is 1,5-diamino-3-azapentane. Peralkylated diamines seem to yield stable Cu^I complexes,[2,7-9] of which [Cu(tmen)$_2$]$^+$ (**2**), where tmen is tetramethylethylenediamine, is a typical case.[8] However, chemical properties of these Cu^I complexes and their CO or olefin adducts (e.g. complex stabilities) in *aqueous* solutions are scanty. A most probable reason is that those tridentate or bidentate amine donors do not sufficiently protect Cu^I from disproportionation to more stable Cu^{II} complexes and Cu^0 in aqueous environments.[11]



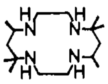
1

[Cu(dien)(CO)]$^+$



2

[Cu(tmen)$_2$]$^+$



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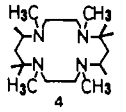

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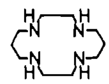

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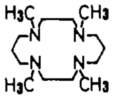

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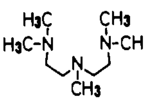
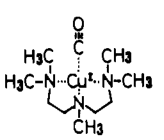


7

pmdien



8

[Cu(pmdien)(CO)]$^+$

Recently it was reported that N-peralkylation of the 14-membered tetraamine macrocycle 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (**3**) to result in compound **4** extremely stabilizes Cu^I complexes of this ligand in *aqueous* solutions even when exposed to air.[4] This result may be relevant to other observations that the N-permethylation of macrocycles **3** and **5** to compounds **4** and **6** also stabilizes lower oxidation state complexes of Ni^I and Pd^I.[12,13] These effects were attributred to one, or more, of the following effects: (i) The N-methylation, due to steric hindrance, increases the cavity of the macrocycle to accommodate larger M^I atoms.[14] (ii) The tertiary amines are poorer σ-donors and hence contribute to the destabilization of M^{II}.[12,14-16] (iii) The N-methylation may create hydrophobic environments, favorable for the lower oxidation state complexes.[12,14] If (ii) and/or (iii) are the dominant factors with those M^I macrocyclic tetradentate complexes, multidentate (higher than bidentate tmen) open-chain amine donors upon N-alkylations may also stabilize Cu^I in aqueous solutions.

We decided, therefore, to study the interaction of Cu^I with pmdien in comparison with that with dien and tmen in *aqueous* solutions (pmdien is 2,5,8-trimethyl-2,5,8-triazanonane (**7**)). Our choice of pmdien was due to the following reasons: (i) The possible tridentate coordination seems most appropriate for Cu^I to be left with a vacancy for a monodentate CO or CH_3CN ligand. (ii) The ligand would be flexible enough to fit the geometric re-

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∥ On sabbatical leave from the Chemistry Department, Ben Gurion University of the Negev, Beer-Sheva, Israel.

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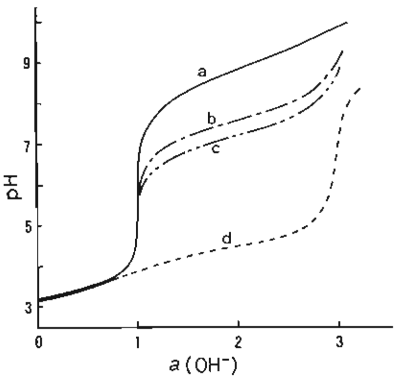

Figure 1. Potentiometric titration curves for L·3HCl (L = pmdien) at 25 °C and I = 0.20 (NaNO$_3$): (a) [total L] = 1.0 × 10^{-3} M only under an Ar atmosphere; (b) [total L] = [total Cu^I] = 1.0 × 10^{-3} M in Ar-saturated 4% v/v CH$_3$CN; (c) [total L] = [total Cu^I] = 1.0 × 10^{-3} M in CO-saturated 10% v/v CH$_3$CN; (d) [total L] = [total Cu^{II}] = 1.0 × 10^{-3} M under an Ar atmosphere. a is the moles of base per mole of pmdien.

quirements of Cu^I and Cu^{II}. (iii) The ligand would have a hydrophobic nature.

Experimental Section

All materials were of analytical reagent grade. The ligand pmdien (**7**) was used as the 3 HCl salt purified by recrystallization from 6 M HCl(aq)/MeOH. [Cu^I(NCCH$_3$)$_4$]ClO$_4$ was prepared as described by Hathaway et al.[17] The various quantitative ratios for CO/Ar atmospheric pressure were obtained by the use of a mass-flow-controlled gas mixer (from Kojima Co.).

Electrochemical measurements were carried out with a Yanaco P-1100 polarographic analyzer and a three-electrode cell. A SCE served as a reference electrode. The pH was measured with an Orion Research 811 pH meter. Potentiometric titrations were carried out as described earlier in detail.[3] UV-visible spectra were recorded on a Hitachi U-3200 spectrophotometer with the syringe technique for anaerobic measurements.[4]

Preparation of [Cu(pmdien)(CO)]ClO$_4$ (8(ClO$_4$)). Treatment of [Cu^I(NCCH$_3$)$_4$]ClO$_4$ (35 mg) with 1 equiv of **7**·3HCl (28.5 mg) and 3 equiv of NaOH in 1 mL of 10% CH$_3$CN/90% H$_2$O under CO for 24 h at 25 °C yields **8** (ClO$_4$) as a colorless crystalline solid (10 mg). This solid is fairly sensitive to air (as judged by the gradual color change to blue). Anal. (for freshly prepared sample). Calcd for C$_9$H$_{23}$N$_3$Cu(ClO$_4$)(CO): C, 32.97; H, 6.36; N, 11.53. Found: C, 32.55; H, 6.60; N, 11.18. IR: ν_{CO} (KBr pellet) 2082 cm^{-1}; ν_{CO} (H$_2$O solution) 2088 cm^{-1}.

Results and Discussion

We have initiated our study with testing the behavior of the Cu^{II}/pmdien system in aqueous solution, which was then polarographically seen to generate stable Cu^I species in the presence of CO or acetonitrile.

Cu^{II}/pmdien System. From the pH-metric titration curve of pmdien in the presence of Cu^{II}SO$_4$ (Figure 1d), we have confirmed the complexation constant for eq 1 as log $K_{Cu^{II}L}$ = 12.3 ± 0.1 at I = 0.2 (NaNO$_3$) and 25 °C, in good agreement with the reported value of 12.16 at I = 0.13 and 25 °C.[18]

$$\mathrm{Cu^{II} + pmdien \rightleftharpoons [Cu(pmdien)]^{2+}} \quad K_{\mathrm{Cu^{II}L}}\ (\mathrm{M^{-1}}) \qquad (1)$$

The polarograms of Ar-saturated solutions containing 4.8 × 10^{-4} M Cu^{II}SO$_4$ and 5.0 × 10^{-2} M pmdien at I = 0.20 (NaNO$_3$ + 0.03 M phosphate), 25.0● 0.1 °C, and pH 6.70–7.91 showed that the 1:1 complex is reduced at E_{exp} = –0.165 to –0.238 V vs SCE by a single two-electron process (see eq 2), where the usual

$$\mathrm{[Cu(pmdien)]^{2+}} + i\mathrm{H^+} + 2\mathrm{e^-} \overset{\mathrm{Hg}}{\rightleftharpoons} \mathrm{Cu(Hg)} + [\mathrm{H}_i\mathrm{(pmdien)}]^{i+} \qquad (2)$$

log-plot slopes are 30 mV/decade and E_{exp} is the redox potential under experimental conditions (see Figure 2a). The cyclic voltammogram (CV) with a hanging-mercury-drop electrode supports the pseudoreversible 2e redox reaction (see Figure 3a). The variation of E_{exp} values for the pmdien system permitted us to determine the log $K_{Cu^{II}L}$ value of 12.2 ± 0.1, which agrees well with the value obtained pH metrically above. This log $K_{Cu^{II}L}$ value and $E°$[Cu^{II}/Cu^0(Hg)] = +0.018 V vs SCE[19] allowed us to calculate the theoretical standard redox potential $E°$([Cu(pmdien)]$^{2+}$/Cu^0(Hg) + pmdien) = –0.343 V vs SCE at 25 °C.

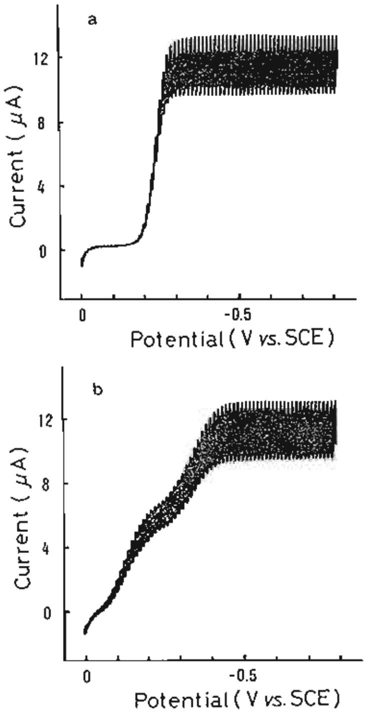

Figure 2. Polarograms of the Cu^{II} (4.8 × 10^{-4} M)/pmdien (5.0 × 10^{-2} M) system at pH 7.3 (0.02 M phosphate), 25 °C, and I = 0.20 (NaNO$_3$): (a) under an Ar atmosphere; (b) under a CO atmosphere.

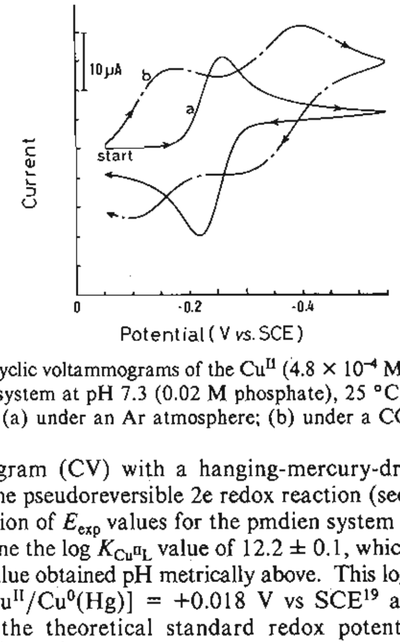

Figure 3. Cyclic voltammograms of the Cu^{II} (4.8 × 10^{-4} M)/pmdien (5.0 × 10^{-2} M) system at pH 7.3 (0.02 M phosphate), 25 °C, and I = 0.20 (NaNO$_3$): (a) under an Ar atmosphere; (b) under a CO atmosphere.

The present result implies that generation of [Cu(pmdien)]$^+$ is very unfeasible in pure aqueous solution.

Cu^{II}/pmdien/CO System. However, when the [Cu(pmdien)]$^{2+}$ aqueous solution was saturated with CO (9.3 × 10^{-4} M at 25 °C[20]), the one-step 2e-reduction wave of [Cu(pmdien)]$^{2+}$ split into two steps (at E_{exp} = –0.151 and –0.350 V vs SCE), each consisting of 1e-reduction processes, while the total redox wave height remained the same (see Figure 2b). The CV (Figure 3b) supports the two consecutive 1e redox reactions. A similar situation occurs with [Cu(tmen)$_2$]$^{2+}$ (**2**) in the absence (E_{exp}([Cu(tmen)$_2$]$^{2+}$/Cu^0(Hg) + 2tmen) = –0.175 V at 5.0 × 10^{-2} M tmen, 1.0 × 10^{-3}

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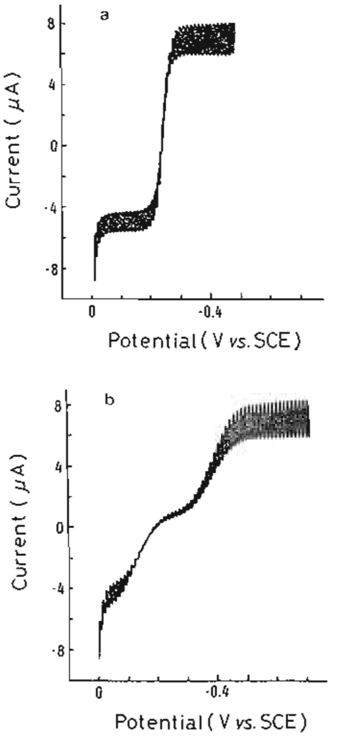

Figure 4. Polarograms of the Cu^I (5.0×10^{-4} M)/pmdien (5.0×10^{-2} M) system in 10% v/v CH_3CN at pH 7.4 (0.02 M phosphate), 25 °C, and $I = 0.20$ ($NaNO_3$): (a) under an Ar atmosphere; (b) under a CO atmosphere.

M Cu^{II}, $I = 0.1$ ($NaClO_4$), 25 °C, and pH 7.3) and presence of a CO atmosphere, where separation of the two consecutive 1e redox waves −0.075 and −0.270 V in CO, is smaller. In anhydrous DMSO solution, similar two-step reduction behaviors were reported with Cu^I/tmen/CO systems.[10] However, such two-step reductions were not seen with the Cu^{II}/dien/CO system, although some turbulence of a 2e-reduction wave was seen (about −0.5 V vs SCE), which suggests a quite unstable nature of $[Cu(dien)(CO)]^+$ (**1**) in aqueous solution. In this case we recall that it is only in methanolic solution that the stable $[Cu(dien)(CO)]^+$ complex (**1**) is formed.[5]

In the log-plot treatments for the Cu^{II}/pmdien/CO system, the reciprocal slopes for the stepwise 1e-reduction wave gave 50 and 55 mV/decade for $Cu^{II} \rightleftarrows Cu^I$ and $Cu^I \rightleftarrows Cu^0$, respectively. Hence, eq 3 and 4, both of which are almost reversible, are considered to occur.

$$[Cu(pmdien)]^{2+} + e^- + CO \rightleftarrows \underset{\mathbf{8}}{[Cu(pmdien)(CO)]^+} \quad (3)$$

$$E_{exp} = -0.151 \text{ V}$$

$$[Cu(pmdien)(CO)]^+ + e^- \overset{Hg}{\rightleftarrows} Cu^0(Hg) + CO + pmdien \quad (4)$$

$$E_{exp} = -0.350 \text{ V}$$

In order to check whether the Cu^I state really intervenes under these conditions, $[Cu^I(NCCH_3)_4]ClO_4$ was used in Ar- or CO-saturated aqueous solutions containing 5×10^{-2} M pmdien at $I = 0.20$ ($NaNO_3$) and pH 7.4. To prevent formation of the yellow precipitate in aqueous solution, $[Cu^I(NCCH_3)_4]ClO_4$ (65 mg) had been first dissolved in CH_3CN (10 mL) under Ar. The final solution contained ca. 5% v/v CH_3CN and 1.0×10^{-3} M Cu^I ion. Two identical (reversible) redox potentials for $Cu^{II} \rightleftarrows Cu^I \rightleftarrows Cu^0$ were observed in the CO-saturated solutions whether starting from Cu^{II} or Cu^I (see Figure 4b). A similar result was obtained when $[Cu^I(NCCH_3)_4]ClO_4$ was initially dissolved in CH_3OH instead of CH_3CN, indicating acetonitrile is not essential to reduce Cu^{II} to Cu^I in the presence of CO.

It was noted during the polarographic studies that the colorless aqueous solution layer in contact with the mercury, which is formed at the bottom of the vessel, changed to dark blue, indicating that the mercury tends to catalyze the possible disproportionation of the colorless Cu^I complexes to blue Cu^{II} complexes and Cu^0-(Hg), in either Ar- or CO-saturated solutions.

Cu^I/pmdien System. In order to determine the stoichiometries of the Cu^I/pmdien system and their complex formation constants, we have conducted the pH-metric titrations of pmdien·3HCl in the presence of Cu^I (as $[Cu^I(NCCH_3)_4]ClO_4$) at varying concentrations of CH_3CN and CO (available by using the CO/Ar gas mixer, see Experimental Section) in aqueous solution. Typical titration curves are shown in Figure 1b,c. The pK_a values of pmdien were unaffected within ±0.02 unit by the concentration change (0–10% v/v) of CH_3CN.

The pH titration experiment for 1.0×10^{-3} M pmdien·3HCl in the presence of equimolar Cu^I (Figure 1b) indicated the 1:1 Cu^I complex formation without significant oxidation to the Cu^{II} complex. The similar pH-metric determination of Cu^I complexation in CH_3CN/H_2O solutions with a macrocyclic N_3S ligand (L″) by Kaden[21] led to $[Cu(L'')]^+$ and $[Cu(L'')(NCCH_3)]^+$ formation. In the present Cu^I/pmdien system, an analogy was drawn as in eq 5 and 6. Moreover, an additional equilibrium

$$Cu^I + pmdien \rightleftarrows [Cu(pmdien)]^+ \quad K_{Cu^IL}\ (M^{-1}) \quad (5)$$

$$[Cu(pmdien)]^+ + CH_3CN \rightleftarrows [Cu(pmdien)(NCCH_3)]^+ \quad K_{AN}\ (M^{-1}) \quad (6)$$

$$[Cu(pmdien)]^+ + CO \rightleftarrows \underset{\mathbf{8}}{[Cu(pmdien)(CO)]^+} \quad K_{CO}\ (M^{-1}) \quad (7)$$

(eq 7) was considered to occur in the CO-containing solution (see Figure 1c). Since most of the $[Cu(pmdien)]^+$ would be expected to shift to more stable $[Cu(pmdien)(NCCH_3)]^+$ or $[Cu(pmdien)(CO)]^+$ (CH_3CN and CO are good π acceptors to stabilize Cu^I states) in the presence of 2–10% v/v CH_3CN and 0–0.93 mM CO, only the overall complexation constants $K_{Cu^IL}K_{AN}$ (= $[[Cu(pmdien)(NCCH_3)]^+]/[Cu^I][pmdien][CH_3CN]$) and $K_{Cu^IL}K_{CO}$ (=$[[Cu(pmdien)(CO)]^+]/[Cu^I][pmdien][CO]$) were calculable, being $(1.7 \pm 0.1) \times 10^{10}$ M^{-2} and $(3.2 \pm 0.1) \times 10^{16}$ M^{-2}, respectively. Evidently, the CO adduct **8** is far more stable than the acetonitrile adduct. The calculation detail is described in the supplementary material. A similar titration of dien with Cu^I failed, due to rapid oxidation (or disproportionation) of $[Cu(dien)]^+$ to the Cu^{II} complex (blue) and Cu^0.

Decomposition Rate of $[Cu(pmdien)(NCCH_3)]^+$ and $[Cu(pmdien)(CO)]^+$. $[Cu(pmdien)]^{2+}$ in 0.1 M $NaClO_4$ aqueous solution at pH 7.4 has an absorption maximum at 660 nm (ε 240) and 292 nm (ε 5400). The increase in the absorbance at 660 nm as the freshly prepared $[Cu(pmdien)(NCCH_3)]^+$ (2.0×10^{-3} M $[Cu^I(NCCH_3)_4]ClO_4$ + 5.0×10^{-2} M pmdien at pH 7.4) is allowed to stand under an Ar atmosphere gives a measure of the lifetime of the Cu^I complex. The lifetime of $[Cu(pmdien)(NCCH_3)]^+$ in Ar-saturated solutions containing 5% v/v CH_3OH is less than 2 h at 25 °C. This decomposition of the Cu^I complex seems mainly due to disproportionation to Cu^{II} and Cu^0, as suggested by the decrease in the total copper ion (Cu^{II} + Cu^I) concentration in the solution as time passes by. Since this disproportionation is an autocatalyzed heterogeneous process, the reproducibility of the measured half-life times was rather poor. Analogous experiments to test the stability of $[Cu(tmen)]_2]^+$ (**2**) in place of pmdien ended in failure due to the immediate formation of a white precipitate (possibly Cu^IOH) even at pH 6.2.

The half-life times are more than 2 weeks (checked by UV absorption) for $[Cu(pmdien)(NCCH_3)]^+$ (2.0×10^{-3} M) in 5% v/v CH_3CN and almost endless for $[Cu(pmdien)(CO)]^+$ in the CO-saturated solution, so as to permit the preceding pH-metric titrations.

An experiment to prepare $[Cu(pmdien)(CO)]^+$ (**8**) solutions via chemical reduction of $[Cu(pmdien)]^{2+}$ (1.0×10^{-3} M $CuSO_4$

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and 0.1 M pmdien) has succeeded by use of ascorbate in CO-saturated solution at pH 10. No reduction of the Cu^{II} complex was possible in the absence of CO. This explains why we did not see the two-step 1e redox reaction in the polarography of the Cu^{II} and Cu^{I} complexes with pmdien in CH_3CN (only)-containing aqueous solution.

Comparison of $[Cu(dien)(CO)]^+$ (1) and $[Cu(pmdien)(CO)]^+$ (8). Finally, **8** was isolated as the crystalline perchlorate salt from *aqueous* solution (see Experimental Section). A molecular model suggests a tetrahedral structure for **8** similar to that established (by X-ray study) for **1**.[5] The colorless solid **8**(ClO_4) gradually turned to blue in the air. However, such oxidation of **8** is apparently slower than that of the previous **1**. The infrared ν_{CO} signals occur at 2082 cm^{-1} (KBr pellet) and 2088 cm^{-1} (in H_2O) for **8** and 2080 cm^{-1} (in THF or Nujol) for **1**,[5] suggesting a common end-on CO bonding to Cu^{I}.[11] CO dissolved in H_2O failed to show a definite ν_{CO} band due to perturbation with H_2O. The ν_{CO} (gas) value is reported at 2170 cm^{-1}.[20] If pmdien were a much weaker σ-donor (or stronger π-acceptor) than dien, we would anticipate a stronger Cu^{I}–CO bonding for **8**, which would be reflected in a higher ν_{CO} value.[22] A characteristic UV absorption in aqueous solution occurs at λ_{max} 275 nm (ϵ 3900) for **8**, while no such UV behaviors in solution were reported for previous Cu^{I}–CO complexes, including **2**.

Concluding Remarks

The present study has disclosed that the tridentate tertiary saturated amine pmdien is an appropriate ligand to sustain Cu^{I} with the aid of a monodentate π-ligand such as CH_3CN or CO in neutral *aqueous* solutions as monomeric, four-coordinate Cu^{I} complexes. The good separation between the two 1e redox systems by **8** may open up some applications such as a new CO-gas sensor.

The results clearly point out that a N-peralkylated tridentate open-chain tertiary amine (pmdien) stabilizes Cu^{I} in aqueous solutions more than the nonalkylated counterpart (dien). A direct comparison of the $[Cu(L)(CO)]^+$ formation constants failed due to the instability of the dien system **1** in aqueous solution. However, a similar ν_{CO} frequency of the Cu^{I}-bound CO indicates similar donor (to Cu^{I}) effects for pmdien and dien. The stability of the Cu^{I}/pmdien system **8** against water or other hostile ligands seems due to the steric and/or hydrophobic effects of permethylation. This result suggests that the analogous effect observed in tetraaza macrocyclic complexes[4,12,13] is not due to an increase of the cavity of the macrocyclic ligand but rather to the steric hindrance and/or hydrophobicity of the methylated ligands.

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Supplementary Material Available: Calculation procedure for Cu^{I} complex formation constants (3 pages). Ordering information is given on any current masthead page.

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(22) The infrared ν_{CO} band for the CO adduct of $[Cu(cimetidine)]^+$ (containing an imidazole ligand)[3] was observed at 2097 cm^{-1} in CO-saturated aqueous solution (Kimura, E.; Koike, T. Unpublished results).

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Syntheses of Pentaammineosmium(III) and -osmium(II) Complexes: Pentaammine(trifluoromethanesulfonato-*O*)osmium(III)

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The triflato complex $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ is prepared in 95–100% yield by either the Br_2 or O_2 oxidation of $[Os(NH_3)_5(N_2)]Cl_2$ in neat CF_3SO_3H or the substitution reaction of $[Os(NH_3)_5Cl]Cl_2$ in neat CF_3SO_3H. Solvation rates are rather rapid in comparison to those of other Os(III) complexes, with $k_{obs} = 8.8 \times 10^{-4}$ s^{-1} at 25 °C in 1 M aqueous CF_3SO_3H. The solvation rate constants have been recorded for a number of solvents; however, basic solvents cause disproportionation reactions, which limits the range of solvents in which this reaction can be studied. In the case of $[Os(NH_3)_5(acetone)]^{3+}$, a second first-order reaction is observed, which is believed to involve the condensation of acetone with an ammine ligand. A large variety of pentaammineosmium(III) complexes can be prepared either by the direct reaction of the triflato complex with the neat ligand or by the use of relatively labile solvent complexes as intermediates. These reactions are not suitable for basic ligands because of the disproportionation problems. Complexes with many anionic ligands are prepared readily by heating the triflato complex in aqueous solutions of HX or acidified NaX solutions. The osmium(II) analogues are prepared readily from the reduction of the osmium(III) complexes. The shifts in the Os(III/II) redox potentials of the complexes containing the π-acid ligands compared to $[Os(NH_3)_6]^{3+/2+}$ are more positive than the corresponding shifts in the ruthenium analogues. This indicates the greater extent of π-back-bonding for Os(II), as compared to Ru(II). The reactivity patterns of the Os(III) and Ru(III) complexes also indicate that π-back-bonding is significant for Os(III), but not for Ru(III). The $[Os(NH_3)_5(acetone)]^{3+/2+}$ and $[Os(NH_3)_5(dmso)]^{3+/2+}$ complexes exhibit oxidation-state-dependent linkage isomerization reactions. The electronic absorption spectra of both the Os(III) and Os(II) complexes with π-acid ligands are dominated by MLCT transitions, which occur at lower energies for the former. The electronic transitions that occur within the t_2 subset of the 5d orbitals are observed in the near-IR region. They are due to the effects of spin–orbit coupling on the t_2^5 electronic configuration and are an order of magnitude more intense for the complexes with π-acid or π-base ligands than those where the ligand shows little or no tendency to π-bond.

Introduction

Although the known chemistry of $[Ru(NH_3)_5L]^{n+}$ in both the Ru(II) and Ru(III) oxidation states is quite extensive, the corresponding osmium chemistry is not as well-known.[1] This disparity has arisen partially from the historical difficulty in preparing osmium(III) pentaammine complexes[1–4] and partially from the instability of many Os(II) complexes to oxidation by water or to ligand reduction.[4–6] In particular, the instability of $[Os(NH_3)_5(OH_2)]^{2+}$ to oxidation by water[5,6] has limited its use as an effective synthetic intermediate, unlike the Ru(II) analogue.

Since it was first shown that the triflato (trifluoromethanesulfonato) ligand of $[Cr(OH_2)_5(OSO_2CF_3)]^{2+}$ is comparable in

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