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# Polymeric Thiolate Complexes in Solution. Solution Equilibria Studies of the Cadmium(II) Complexes of 3-(Dimethylamino)-1-propanethiol and Comparative Study with Other Aliphatic γ-Mercapto Amines

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Polynuclear complex formation between Cd(II) and 3-(dimethylamino)-1-propanethiol has been studied by means of 382 emf measurements with a glass electrode in 7 separate titrations at 25 °C in 3 M $NaClO_4$ medium (10% (v/v) $CH_3OH$). Conclusions drawn from the graphical methods based on the "core + links" hypothesis and on the "extended variation method" agree with the results obtained from the numerical treatment. Experimental data at $3 < pH < 11$ can be explained by assuming that the following complexes predominate in a wide pH range: $[Cd(HA)_4]^{2+}$, $[Cd_3(HA)_6]^{6+}$, $[Cd_3(HA)_8]^{6+}$, $[Cd_4(HA)_9]^{8+}$, and $[Cd_4(HA)_{10}]^{8+}$, HA being the uncharged ligand. The deprotonation of these species gives rise to several mononuclear and polynuclear ternary complexes $Cd_pA_qH_r$ ($r < q$), A denoting the completely deprotonated ligand. Experimental data suggest that chelate formation does not take place. The stoichiometries of the $[Cd_p(HA)_q]^{2p+}$ soluble species found in several Cd(II)–aliphatic γ-mercapto amine systems are compared, and their possible geometry is analyzed. The influence of the flexibility of the hydrocarbon chain and of the degree of substitution on the amine function as factors affecting the chelating ability of γ-mercapto amines is discussed.

## Introduction

One of the main reasons for the actual evolution of the fundamental coordination chemistry of metal–simple thiolate complexes[2-4] is that they can be a very good reference when investigating the chemistry of metalloproteins.[4-6] It is surprising however, that while many efforts have been devoted to finding new synthetic strategies[4,8-11] and topological structural relationships[12] for solid metal–thiolate complexes as as well as to using them as synthetic precursors of metal–sulfide–thiolate clusters,[4,13] very few solution equilibria studies have been reported.[14] Among those, $^{113}$Cd NMR studies,[15] mainly with the aim of characterizing structurally the $Cd_3$ and $Cd_4$ clusters already reported for Cd metalloproteins,[16] predominate clearly.

The polymeric nature of neutral metal–simple thiolate complexes and consequently their low solubility in aqueous media render solution equilibria studies as well as crystal formation for X-ray structure determination difficult. The need to introduce a solubilizing group in the thiol molecule led us in the past to choose γ-mercapto amines as models for the behavior of simple thiol ligands. The coordinating ability of the amine group depends on its degree of substitution, and it is suppressed if the complexed ligand is in a zwitterionic form.[17] The structures of several thiolate complexes with 4-mercapto-1-methylpiperidine (4-MP)[18] and 3-(dimethylamino)-1-propanethiol (MMA)[19] show that under certain experimental conditions coordination proceeds exclusively via the thiol function. Also, the stoichiometric coefficients of soluble $[M_x(SR)_y]^{x+}$ complex species with 4-MP[20] and 3-amino-1-propanethiol (MPA)[21] ligands suggest that those species can be considered as short fragments of an infinite polymeric chain analogous to that found in $[Cd(4\text{-}MP)_2]_n^{2n+}$.[18a] Up to now, no evidence for the adamantane-like cage structure, frequently encountered in thiolate complexes,[22] has been found while working with aliphatic γ-mercapto amines in aqueous media. These two main features, the aliphatic nature of the "thiol" ligands and the possibility of working in aqueous media, give a new and possibly more closely related approach to the sought relationship between thiolate complexes and metal binding by metalloproteins.

As a part of our continuing interest in γ-mercapto amine complexes and because of the special relevance of Cd(II) in biological systems[23] we undertook a detailed potentiometric study of the Cd(II)–MMA system. In this paper we report the stoichiometry and corresponding formation constants of soluble species found in a wide pH range and over a range of total concentrations. In addition, a comparison of the behavior of 4-MP, MPA, and

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[1] Present address: Diversey, SAE, 08213 Polinyà, Barcelona, Spain.

[2] Dance, I. G. *Polyhedron* **1986**, *5*, 1037 and references therein.

[3] Blower, P. J.; Dilworth, J. R. *Coord. Chem. Rev.* **1987**, *76*, 121 and references therein.

[4] Watson, A. D.; Rao, Ch. P.; Dorfman, J. R.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 2820 and references therein.

[5] Coucouvanis, D.; Swenson, D.; Baenziger, N. C.; Murphy, C.; Holah, D. G.; Sfarnas, N.; Simopoulous, A.; Kostikas, A. *J. Am. Chem. Soc.* **1981**, *103*, 3350 and references therein.

[6] Holm, R. H. *Chem. Soc. Rev.* **1981**, *10*, 455 and references therein.

[7] Kojima, Y.; Berger, C.; Kägi, J. H. R. In *Metallothionein*; Kägi, J. H. R., Nordberg, M., Eds.; Birkhäuser: Basel, Switzerland, 1979; pp 153–161.

[8] Reference 2, pp 168–170.

[9] Rosenfield, S. G.; Armstrong, W. H.; Mascharak, P. K. *Inorg. Chem.* **1986**, *25*, 3014.

[10] Tang, K.; Aslam, M.; Block, E.; Nicholson, T.; Zubieta, J. *Inorg. Chem.* **1987**, *26*, 1488.

[11] Said, F. F.; Tuck, D. G. *Inorg. Chim. Acta* **1982**, *59*, 1.

[12] Reference 1, pp 1083–1087.

[13] Pulla Rao, Ch.; Dorfman, J. R.; Holm, R. H. *Inorg. Chem.* **1986**, *25*, 428.

[14] Avdeef, A.; Brown, J. A. *Inorg. Chim. Acta* **1984**, *91*, 67.

[15] (a) Dance, I. G. *Inorg. Chim. Acta* **1985**, *108*, 227. (b) Dance, I. G.; Saunders, J. K. *Ibid.* **1985**, *96*, L71. (c) Carson, G. K.; Dean, P. A. W.; Stillman, M. J. *Ibid.* **1981**, *56*, 59. (d) Baumann, G. C.; Summers, M. F.; Hutchinson, J. P.; Zubieta, J.; Marzilli, L. G. *Inorg. Chem.* **1984**, *23*, 3104. (e) Haberkorn, R. A.; Que, L., Jr.; Gillum, W. O.; Holm, R. H.; Liu, C. S.; Lord, R. C. *Ibid.* **1976**, *15*, 2408.

[16] (a) Otvos, J. D.; Armitage, I. M. *J. Am. Chem. Soc.* **1979**, *101*, 7734. (b) Otvos, J. D.; Armitage, I. M. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 7094. (c) Lacelle, S.; Stevens, W. C.; Kurtz, D. M., Jr.; Richardson, J. W., Jr.; Jacobson, R. A. *Inorg. Chem.* **1984**, *23*, 930.

[17] Dance, I. G.; Guerney, P. J.; Rae, A. D.; Scudder, M. L.; Baker, A. T. *Aust. J. Chem.* **1986**, *39*, 383.

[18] (a) Bayón, J. C.; Briansó, M. C.; Briansó, J. L.; González-Duarte, P. *Inorg. Chem.* **1979**, *18*, 3478. (b) Gaete, W.; Ros, J.; Solans, X.; Font-Altaba, M.; Briansó, J. L. *Ibid.* **1984**, *23*, 39. (c) Briansó, M. C.; Briansó, J. L.; Gaete, W.; Ros, J.; Suñer, C. *J. Chem. Soc., Dalton Trans.* **1981**, 852. (d) Barrera, J.; Bayón, J. C.; González-Duarte, P.; Sola, J.; Viñas, J. M.; Briansó, J. L.; Briansó, M. C.; Solans, X. *Polyhedron* **1982**, *1*, 647.

[19] (a) Barrera, H.; Bayón, J. C.; Suades, J.; Germain, C.; Declerq, J. P. *Polyhedron* **1984**, *3*, 969. (b) Casals, i.; González-Duarte, P.; Sola, J.; Font-Bardia, M.; Solans, J.; Solans, X. *J. Chem. Soc., Dalton Trans.* **1987**, 2391. (c) González-Duarte, P.; Sola, J.; Vives, J.; Solans, X. *J. Chem. Soc., Chem. Commun.* **1987**, 1641. (d) Casals, I.; González-Duarte, P.; Sola, J.; Miravitlles, C.; Molins, E. *Polyhedron*, in press.

[20] (a) Bayón, J. C.; González-Duarte, P. *J. Chem. Soc., Dalton Trans.* **1982**, 487. (b) Bayón, J. C.; González-Duarte, P.; Vives, J. *Ibid.* **1984**, 2671.

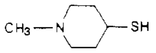
[21] González-Duarte, P.; Vives, J. *J. Chem. Soc., Dalton Trans.*, in press.

[22] (a) Dance, I. G.; Choy, A.; Scudder, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 6285. (b) Holm, R. H.; Hagen, K. S. *Inorg. Chem.* **1983**, *22*, 3171. (c) Dean, P. A. W.; Vittal, J. J.; Payne, N. C. *Ibid.* **1987**, *26*, 1683 and references therein.

[23] (a) Kostial, K. In *Trace Elements in Human and Animal Nutrition*, 5th ed.; Mertz, W., Ed.; Academic Press: New York, 1986; Vol. 2, pp 319–345. (b) Karin, M.; Haslinger, A.; Holtgreve, H.; Richards, R. I.; Krauter, P.; Westphal, H. M.; Beato, M. *Nature* **1984**, *308*, 513.

0020-1669/89/1328-0025$01.50/0

**Table I.** Glossary of Terms and Symbols

| | |
|---|---|
| MMA | $(CH_3)_2N(CH_2)_3SH$ |
| MPA | $H_2N(CH_2)_3SH$ |
| 4-MP |  |
| $H_2A$ | $(CH_3)_2HN^+(CH_2)_3SH$ |
| HA | monoprotonated form of ligand that can exist in two diff forms: $(CH_3)_2HN^+(CH_3)_2S^-$ (zwitterionic form) and $(CH_3)_2N(CH_2)_3SH$; complexed HA ligand denotes zwitterionic form exclusively |
| A | $(CH_3)_2N(CH_2)_3S^-$, completely deprotonated form of ligand |
| $M_t$ | total concn of metal |
| $L_t$ | total concn of ligand |
| [H] | free H concn |
| $H_t$ | total concn of H |
| $\bar{j}$ | av no. of monoprotonated ligands, HA, bound per metal, calcd from exptl data according to<br>$\bar{j} = \frac{H_t - [H] + K_w[H]^{-1}}{L_t}$ |
| $\bar{n}$ | av no. of monoprotonated ligands, HA, bound per metal, calcd from exptl data according to<br>$\bar{n} = \frac{L_t(\bar{j} - X)}{M_t(1 - X)} \qquad X = \frac{2[H]^2 + K_1[H]}{[H]^2 + K_1[H] + K_1K_2}$ |
| $t$ | numerical ratio of ligand to metal in links of core + links complexes $Cd[Cd(HA)_t]_x$, or $B(BA_t)_n$ in Sillén's nomenclature, calcd according to<br>$t = (\delta \log M_t/\delta \log [HA])_{\bar{n}}$ |
| $\bar{n}_c$ | the Bjerrum formation function, in a ternary syst, assuming complex species are of the type $Cd_pA_qH_0$<br>$\bar{n}_c = \frac{L_t(1 - Y\bar{j})}{M_t} \qquad Y = \frac{[H]^2 + K_1[H] + K_1K_2}{2[H]^2 + K_1[H]}$ |
| $l$ | completely deprotonated free ligand concn in a ternary syst, assuming that complex species are of the type $Cd_pA_qH_0$<br>$l = \frac{(L_t - \bar{n}_cM_t)K_1K_2}{[H]^2 + K_1[H] + K_1K_2}$ |
| $\bar{p}$, $\bar{q}$, $\bar{r}$ | av stoichiom coeff of $Cd_pA_qH_r$ complexes existing in soln<br>$\bar{p} = \frac{M_t - [Cd^{II}]}{S} \qquad \bar{q} = \frac{L_t - [A]}{S} \qquad \bar{r} = \frac{H_t - [H] + K_w[H]^{-1}}{S}$<br>where $S$ = Sillén's complexity sum = sum of the concns of all complex species existing in soln |
| $\alpha$ | fraction of $Cd^{II}$ complexed in the various $Cd_pA_qH_r$ species, or $p[Cd_pA_qH_r]/M_t$ |
| $K_1K_2$ | ligand acid dissociation const<br>$H_2A \xrightarrow{K_1} HA \xrightarrow{K_2} A$ |
| $K$ | first acidity const of $Cd_p(HA)_q$ species |
| $\Psi_{p,q}$ | complex-formation const according to the reacn<br>$p\mathrm{Cd} + q\mathrm{HA} \rightarrow Cd_p(HA)_q$ |
| $\beta_{p,q,r}$ | stoichiom overall stability const of $Cd_pA_qH_r$ species, related to $\Psi_{p,q}$ and $K_2$, according to<br>$\beta_{p,q,r} = \Psi_{p,q}K_2^{-q}$ |

MMA ligands toward Cd(II) is made. The different chelating abilities shown by $\beta$- and $\gamma$-mercapto amines is also discussed.

A glossary of terms and symbols used throughout the text is given in Table I.

## Experimental Section

**Reagents.** An acidified stock solution of cadmium perchlorate (Alfa) was prepared and standardized as indicated elsewhere.[20b] MMA was synthesized from 3-amino-1-propanol (Fluka) according to the literature[24] and purified by several distillations under reduced pressure (40 °C at 10 mmHg) until its purity, checked by iodometric determination of the thiol group, was greater than 99.5%. Acidified solutions of the ligand were kept for several weeks without evidence of oxidation. Stock solutions of sodium perchlorate and of sodium hydroxide and perchloric acid in a 3 M (sodium) perchlorate medium (+10% (v/v) $CH_3OH$) were prepared and analyzed according to known procedures.[20a] Methanol (p.a.) was used without further purification.

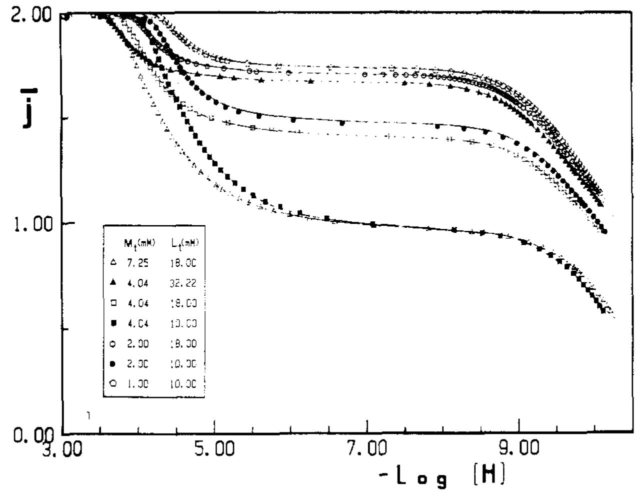


**Figure 1.** Average number of protons bound to the ligand, $\bar{j}$, as a function of log [H] at different ligand to metal ratios. The lines drawn were calculated from the constants in Table IV.

**Apparatus.** The standardization of the glass electrode (Ingold HA 201) and the preparation of the Ag-AgCl reference electrode as well as the "Wilhelm" glass apparatus used for the salt bridge and reference half-cell have already been described.[20a] The computerized titrator used (HP-85) commanded four Hamilton microburets, Model Microlab M, and a Crison potentiometer, Model Digilab 517 (±0.1 mV). The titrations were performed at constant temperature, 25.0 ± 0.1 °C, and under a nitrogen atmosphere.

**Titration Procedure.** Solution equilibria studies of the system MMA–Cd(II) in 3 M (sodium) perchlorate medium (+10% (v/v) $CH_3OH$) have been carried out by means of several series of potentiometric titrations in which the total concentration of metal, $M_t$, and that of the ligand, $L_t$, were held constant; $M_t$ was varied in the range 1–7.25 mM and $L_t$ according to the molar ratio $2.5 < L_t/M_t < 10$. Each series was formed by a set of titrations with the same value of either $M_t$ or $L_t$. The cell used for the emf measurements as well as the titration procedures followed in order to determine the acidity constants of the ligand and the formation constants of the soluble species are analogous to those used in previous studies.[20,21] An additional cadmium amalgam electrode has not been used because of its poor accuracy at free metal concentrations lower than $10^{-6}$ M.[20b]

## Calculations and Results

**Acid Dissociation Constants of the Cation 3-(Dimethylammonio)-1-propanethiol from Emf Data.** Three potentiometric titrations were carried out. It was assumed that species present in solution were of the type $H_jA$ (charges are omitted throughout for clarity), where $j$ is a integer ($0 \leq j \leq 2$) and A denotes the completely deprotonated ligand. The acid dissociation constants were calculated with the program SUPERQUAD,[25] by using a VAX/VMS computer, from 121 pairs of the values log [H] and $\bar{j}$, where [H] and $\bar{j}$ denote respectively the concentration of free hydrogen ion and the average number of protons bound. The methods used to calculate log [H], $\bar{j}$, and $K_w$ in the medium used (p$K_w$ = 14.16) have already been reported.[26] Values found, with the standard deviation of the least significant digit in parentheses, are the following: $H_2A \rightleftharpoons HA + H$, p$K_1$ = 9.87 (1); $HA \rightleftharpoons A + H$, p$K_2$ = 11.24 (1).

**Cadmium Complex Formation Constants from Emf Data.** Seven potentiometric titrations were carried out. Assuming that the complex species present in solution were of the type $Cd_pA_qH_r$, where $p \geq 1$, $q \geq 1$, and $r$ is an integer, values for log [H] and $\bar{j}$, the average number of protons bound to the complexed ligand, were calculated as previously indicated.[21] Plots of $\bar{j}$ against −log [H] corresponding to the seven titrations (Figure 1) show that complexation starts at pH ≈ 3.5, which compares with the value for the system 4-MP–Cd(II)[20b] very well, and that, for any $L_t/M_t$

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[24] Cossar, B. C.; Fournier, J. O.; Fields, D. L.; Reynolds, D. D. *J. Org. Chem.* **1962**, *27*, 93.

[25] Gans, P.; Vacca, A.; Sabatini, A. *J. Chem. Soc., Dalton Trans.* **1985**, 1195.

[26] Barrera, H.; Bayón, J. C.; González-Duarte, P.; Sola, J.; Vives, J. *Talanta* **1983**, *30*, 537.

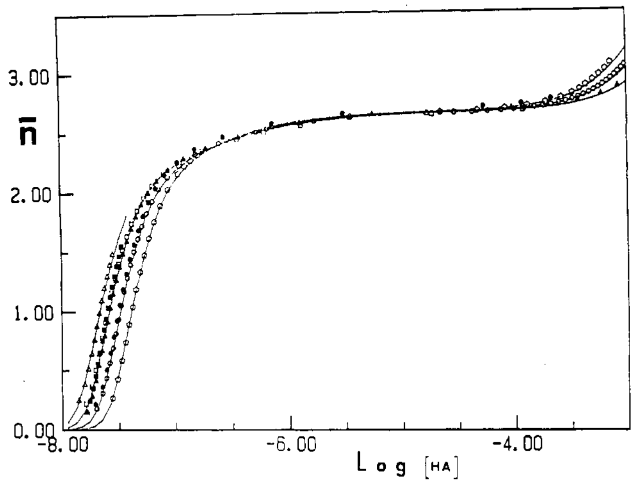

**Figure 2.** Formation curve for $Cd_p(HA)_q$ species at different ligand to metal ratios. The lines drawn were calculated from the constants in Table IV. For the key to the symbols, see Figure 1.

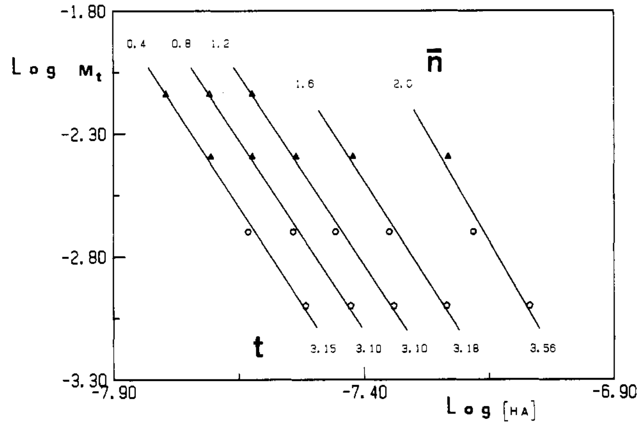

**Figure 3.** Variation of total concentration of Cd(II) with that of the free monoprotonated ligand for several $\bar{n}$ values. The straight lines were calculated by linear regression. For the key to the symbols, see Figure 1.

ratio, the second deprotonation of the ligand takes place at pH $\approx 8.5$. This together with the fact the monoprotonated form of the uncomplexed ligand, HA, starts deprotonation at pH $\approx 9.5$ indicates that the chelating ability of this ligand is low. Also, curves of $\bar{j}$ vs log [H] show a plateau at either $\bar{j} > 1.35$ or $\bar{j} < 1.35$ depending on whether $L_t/M_t$ is respectively greater or smaller than 4. It can be shown that if $\bar{j} = 1.35$, then $[A]/L_t \leq 0.05$, [A] denoting the free, completely deprotonated ligand concentration. Consequently, the experimental points can be divided into two sets and treated analogously to those of the system MPA–Cd(II).[21] Owing to that, only the results will be given here.

**Species of Formula $Cd_p(HA)_q$. Graphical and Numerical Treatment.** Experimental points with $\bar{j} \geq 1.35$ correspond to species of formula $Cd_pA_qH_q$, and thus the system can be considered as a two-component one, in agreement with the formation curves, given in Figure 2, and with results found with other γ-mercapto amines.[20,21]

Graphical treatment (Figure 3) based on the "core + links" hypothesis[27] for the polynuclear complexes gave different results depending on $\bar{n}$, the average number of monoprotonated ligands bound per metal. Thus, while for the range $0.4 < \bar{n} < 1.6$, $t$, the numerical ratio of ligand to metal in links of core + links complexes $Cd[Cd(HA)_t]_x$, and its standard deviation have the values $t = 3.13$ and $\sigma = 0.04$, when the range considered is $0.4 < \bar{n} < 2.0$, those values are $t = 3.22$ and $\sigma = 0.17$. This is due to the high value of $t$ when $\bar{n} = 2.0$ ($t = 3.55$). These results as well as the unequal separation between the formation curves indicate the coexistence of several core + links families for $\bar{n} < 2.5$, or when free metal concentration is not negligible.[20b,21]

The numerical method used[21] together with the limiting conditions imposed led us to the set of $Cd_p(HA)_q$ species given in Table II, indicating that members of two core + links series, $Cd[Cd(HA)_3]_n$ and $Cd_4(HA)_8[Cd(HA)_3]_n$, besides the complexes $Cd_3(HA)_7$ and $Cd_4(HA)_{10}$, these two being responsible for the $t$ values greater than 3, could be present in solution. These results and the comparison of the shape of the curves $\bar{n}$(log [HA]) with those of closely related systems[20b,21] allowed us to conclude that up to $\bar{n} = 2.8$ the core + links families $Cd[Cd(HA)_3]_n$ ($n_{max} = 7$) and $(HA)_2[Cd(HA)_2]_n$ ($n_{max} = 5$), together with mononuclear complexes, were the most likely species. By means of the program SUPERQUAD the final set of $Cd_p(HA)_q$ species and corresponding formation constants were found (Table III).

**Table II.** Set of Possible $p$, $q$ Values for $Cd_p(H)_q$ Species That Meet the Requirements $p_{max} = 7$, $\bar{n}_{max} = 2.55$, and $2.71 < t < 3.73$

| | p | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2 | 3 | 3 | 4 | 4 | 4 | 5 | 5 | 6 | 6 | 7 |
| q | 3 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 14 | 15 | 17 |

**Table III.** Cadmium Complex-Formation Constants According to the Reaction $p$Cd + $q$HA $\rightleftharpoons Cd_p(HA)_q$

| $p$ | $q$ | log $\Psi_{p,q}$[a] | $p$ | $q$ | log $\Psi_{p,q}$[a] |
|---|---|---|---|---|---|
| 3 | 6 | 49.9 | 3 | 8 | 63.8 |
| 4 | 9 | 75.3 | 1 | 4 | 23.1 |
| 4 | 10 | 81.8 | | | |

[a] $\Psi_{p,q}$ is related to the stoichiometric overall stability constant by the relationship $\beta_{p,q,q} = \Psi_{p,q}K_2^{-q}$. The value of $K_2$ is given in the text.

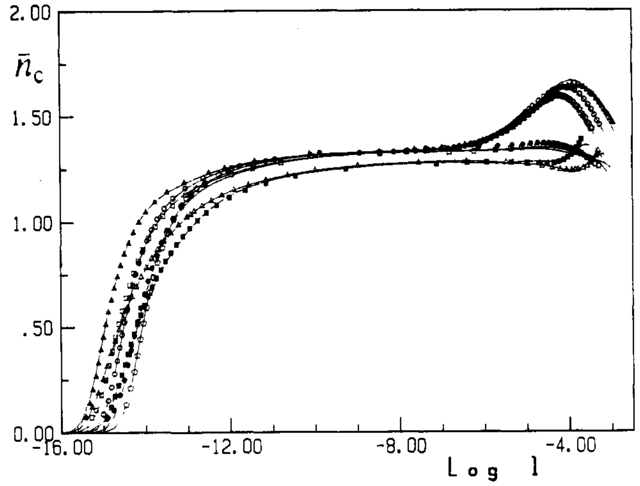

**Figure 4.** Average number of completely deprotonated ligands bound per Cd(II), $\bar{n}_c$, as a function of the calculated concentration of free completely deprotonated ligand, $l$, at different ligand to metal ratios. The lines drawn were calculated from constants in Table IV. For the key to the symbols, see Figure 1.

**Species of Formula $Cd_pA_qH_r$. Graphical and Numerical Treatment.** The existence of ternary complexes of formula $Cd_pA_qH_r$ ($r < q$) in all the pH ranges studied was deduced from the shape of the curves $\bar{n}_c$ vs log $l^{21}$ (Figure 4), $\bar{n}_c$ and $l$ denoting respectively the average number of completely deprotonated ligands bound per metal and the calculated concentration of free, completely deprotonated ligand. Both magnitudes were calculated as already indicated,[21] with all the experimental data taken into account. The decrease in the number of ligands bound at increasing free ligand concentration has also been found in solutions where protonated and deprotonated complex species coexist.[14] In order to widen the information about the system, the "average composition of species in solution" method[28] was used and the

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(27) (a) Sillén, L. G. *Acta Chem. Scand.* **1954**, *8*, 299. (b) Sillén, L. G. *Ibid.* **1954**, *8*, 318.

(28) Avdeef, A. *Inorg. Chem.* **1980**, *19*, 3081.

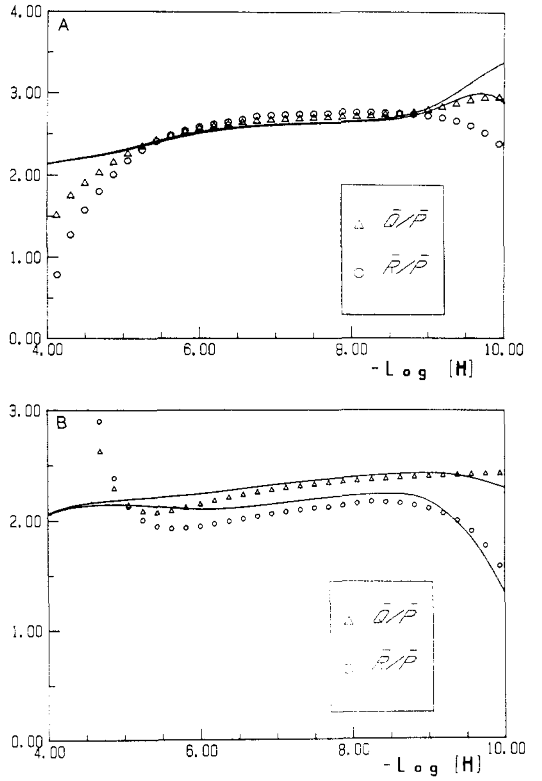

**Figure 5.** Number of bound ligands and hydrogen atoms per metal ion, $\bar{q}/\bar{p}$ and $\bar{r}/\bar{p}$, respectively, as a function of pH for the "common point" titrations: (A) $L_t$ = 18.00 mM, $M_t$ = 4.04 mM; (B) $L_t$ = 10.00 mM, $M_t$ = 4.04 mM. The lines drawn were calculated from the constants in Table IV.

normalized curves $\bar{q}/\bar{p}$ and $\bar{r}/\bar{p}$ vs pH were plotted for the "common point" solutions (Figure 5). While for solutions in which $L_t/M_t > 4$ (Figure 5A) monoprotonated species start deprotonation at pH ≈ 8.5, in solutions where $L_t/M_t < 4$ (Figure 5B) complex species have an average proton to ligand ratio smaller than 1 from pH ≈ 6 onward while increasing the number of ligands bound.

Both graphical representations are compatible with the assumption that the first species formed have the formula $Cd_pA_qH_q$ and that these species, at a pH value depending on the $L_t/M_t$ ratio, start a second deprotonation, giving rise to $Cd_pA_qH_r$ species, where $r < q$. As a consequence the stoichiometry of the $Cd_pA_qH_r$ species depends on that of the existing $Cd_pA_qH_q$ complexes at that particular pH value. Evidently, when $L_t/M_t < 4$ monoprotonated and completely deprotonated species have to coexist from relatively low pH values. Both sets of curves also indicate that no chelation occurs as the second deprotonation of the ligand, which is shown by a decrease in the $\bar{r}/\bar{p}$ curves, is not accompanied by a diminution in the number of complexed ligands. If chelation took place, some ligands would displace others and thus a parallel decrease in the $\bar{q}/\bar{p}$ curves should be observed.

In order to develop an equilibrium model that consisted a minimum number of species and was consistent with the graphical information, it was necessary to carry out the mathematical treatment of the experimental data in several steps. Otherwise the program[25] used could not have refined the great number of possible complexes; each $Cd_pA_qH_q$ species might generate at least $q$ different complexes and corresponding formation constants. The method followed[21] consisted essentially of treating the experimental curves corresponding to high $L_t/M_t$ ratios first, as under these conditions predominating species were those already found when the system was considered as a two-component one. Then, while the rest of the curves were treated, the set of species and constants previously found were included as a fixed contribution. In the third and last stage all the equilibrium constants were refined simultaneously. The final set of species and constants together with the statistical data characteristic of the refinement is given in Table IV. The low value found for $\sigma$ agrees well with the successful simulation of the formation curves and the acceptable reproduction of the normalized coefficients, as indicated by the solid curves in Figures 1, 2, and 4 and Figure 5, respectively.

**Table IV.** Cadmium Complex-Formation Constants[a] for the Species $Cd_pA_qH_r$ at 25 °C and $I$ = 3.0 M ($NaClO_4$) from SUPERQUAD[25]

$$p\text{Cd} + q\text{A} + r\text{H} \rightleftharpoons \text{Cd}_p\text{A}_q\text{H}_r$$

| | $p$ | $q$ | $r$ | $\log \beta_{p,q,r}$ |
|---|---|---|---|---|
| a | 3 | 6 | 6 | 117.33 ± 0.07 |
| b | 4 | 9 | 9 | 176.41 ± 0.05 |
| c | 4 | 10 | 10 | 194.12 ± 0.09 |
| d | 3 | 8 | 8 | 153.65 ± 0.04 |
| e | 1 | 4 | 4 | 68.01 ± 0.02 |
| f | 3 | 6 | 5 | 111.9 ± 0.1 |
| g | 3 | 6 | 2 | 85.19 ± 0.06 |
| h | 4 | 9 | 8 | 170.38 ± 0.07 |
| i | 4 | 10 | 9 | 186.38 ± 0.07 |
| j | 3 | 8 | 7 | 143.4 ± 0.2 |
| k | 3 | 8 | 5 | 123.6 ± 0.2 |
| l | 1 | 4 | 3 | 57.80 ± 0.05 |
| m | 1 | 4 | 2 | 47.2 ± 0.2 |

[a] A denotes the ligand MMA in its completely deprotonated form, $(CH_3)_2N(CH_2)_3S^-$. The number of points is 382, from 7 separate titrations. Estimated variances of the electrode and volume readings are respectively $\sigma_E$ = 0.1 mV and $\sigma_v$ = 0.01 mL. Sample standard deviation $\sigma$ = 4.74. $\sigma_E$, $\sigma_v$, and $\sigma$ are defined as indicated in ref 25.

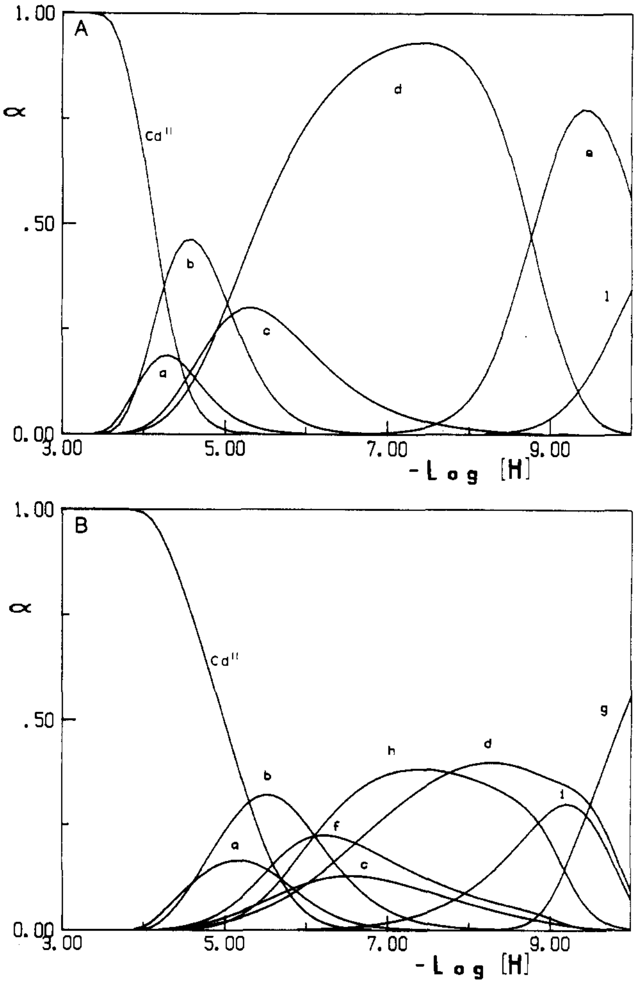

**Figure 6.** Distribution of species as a function of pH: (A) $L_t$ = 30.00 mM, $M_t$ = 4.00 mM; (B) $L_t$ = 10.00, $M_t$ = 4.00 mM. Species whose concentration is lower than 10% have been omitted. For the key to the symbols, see Table IV.

## Discussion

**Soluble Complex Species Formed by Cadmium(II) and 3-(Dimethylamino)-1-propanethiol.** The distribution of species as a function of pH (Figure 6) shows the great dependence of the

**Table V.** Stoichiometry of $Cd_p(HA)_q$ Complex Species Found with MMA, 4-MP,[20b] and MPA[21] Ligands Together with the Corresponding Overall Formation Constants, $\beta_{p,q,r}$ ($r = q$), in 3 M $NaClO_4$ Medium (+10% (v/v) $CH_3OH$) at 25 °C

| MMA-Cd(II) | | 4-MP-Cd(II) | | MPA-Cd(II) | |
|---|---|---|---|---|---|
| $p,q$ | $\log \beta$ | $p,q$ | $\log \beta$ | $p,q$ | $\log \beta$ |
| 1,4 | 68.01 ± 0.02 | 1,4 | 68.4 ± 0.1 | 1,3 | 54.15 ± 0.03 |
| 3,6 | 117.33 ± 0.07 | 3,6 | 116.6 ± 0.1 | 1,4 | 67.39 ± 0.05 |
| 3,8 | 153.60 ± 0.04 | 3,8 | 152.5 ± 0.1 | 3,8 | 152.65 ± 0.03 |
| 4,9 | 176.41 ± 0.05 | 4,9 | 175.5 ± 0.1 | 4,8 | 156.86 ± 0.03 |
| 4,10 | 194.12 ± 0.09 | 4,10 | 193.8 ± 0.1 | 5,12 | 233.27 ± 0.03 |

**Table VI.** Acidity Constant, $K$, of $Cd_p(HA)_q$ Species According to the Reaction $Cd_pA_qH_q \rightleftharpoons Cd_pA_qH_{q-1} + H$, Calculated from the Relationship $K = \beta_{p,q,q-1}/\beta_{p,q,q}$[a]

| | $\log K$ |
|---|---|
| $(3,6,6) \rightleftharpoons (3,6,5) + H^+$ | −5.43 |
| $(4,9,9) \rightleftharpoons (4,9,8) + H^+$ | −6.03 |
| $(4,10,10) \rightleftharpoons (4,10,9) + H^+$ | −7.74 |
| $(3,8,8) \rightleftharpoons (3,8,7) + H^+$ | −10.2 |
| $(1,4,4) \rightleftharpoons (1,4,3) + H^+$ | −10.21 |

[a] $Cd_p(HA)_q$ species are denoted as $(p,q,q)$.

composition of the solution on the ligand to metal ratio. Thus, under excess-ligand conditions (Figure 6A, $L_t/M_t > 4$) there is a predominance of polynuclear over mononuclear species and practically all soluble species can be represented by the formula $Cd_p(HA)_q$. It has already been proposed[20,21] that bound ligands in $M_p(HA)_q$ (M = Zn(II),[20a] Cd(II)[20b]) complexes are in a zwitterionic form and coordinate by the sulfur atom exclusively. Also, the existing species $[Cd_3(HA)_6]^{6+}$, $[Cd_4(HA)_9]^{8+}$, $[Cd_4(HA)_{10}]^{8+}$, $[Cd_3(HA)_8]^{6+}$, and $[Cd(HA)_4]^{2+}$ have the same stoichiometry as that found in the 4-MP–Cd(II) system[20b] (Table V). The predominance of $[Cd_3(HA)_8]^{6+}$ species over a wide pH range explains the high values of $t$ found in the corresponding region, and it also accounts for the solubility of Cd(II)–MMA complex species, as will be discussed later.

The great stability of the $[Cd_3(HA)_8]^{6+}$ species is also shown in Figure 6B, where despite the fact that the ratio $L_t/M_t$ = 10.00/4.00 is inferior to that of ligand to metal in the complex, 8/3, this species is still present in solution in a relatively wide pH range. For a 10/4 ligand to metal mole ratio (Figure 6B) only polynuclear species are detected. The general pattern followed is that once $Cd_p(HA)_q$ complexes are formed, at higher pH values they deprotonate, giving rise to $Cd_pA_qH_r$ species, among which those with $r = q - 1$ predominate. Thus, the first acidity constant of $Cd_p(HA)_q$ species, $K$, can be easily calculated from the overall formation constants (Table VI). If previous assumptions about the structure of soluble species[20,21] are accepted, cadmium atoms in $Cd_4A_{10}H_9$, $Cd_3A_8H_7$, and $CdA_4H_3$ are probably coordinated only to sulfur atoms while in $Cd_3A_6H_5$ and $Cd_4A_9H_8$ it is difficult to decide whether coordinated solvent molecules in $[Cd_3(HA)_6]^{6+}$ and $[Cd_4(HA)_9]^{8+}$ have deprotonated or if the ligand behaves as a chelating agent. The IR spectrum of the solid complex $[Cd(MMA)_2]$,[29] isolated from a solution containing the potassium salt of the ligand and $Cd(ClO_4)_2{\cdot}6H_2O$ in ethanol,[30] clearly indicates that the nitrogen atom does not participate in coordination. Consequently, the second hypothesis seems less likely.

The proximity between the first acidity constants of $[Cd_3(HA)_8]^{6+}$ and $[Cd(HA)_4]^{2+}$ (see Table VI) and that calculated for the amine group of the ligand, $-N^+H(CH_3)_2$, p$K$ = 10.6 by means of Adams' equations,[26] may explain the coexistence of several species $Cd_3A_8H_7$, $Cd_3A_8H_5$, $CdA_4H_3$, and $CdA_4H_2$, at pH ≈ 10. However, the fact that the number of experimental points corresponding to solutions containing these species is relatively small and the fact that all of them under our experimental conditions are present at low concentrations (below 10% in Figure 6B) make us take the number of protons as well as the corresponding formation constants given in Table IV for the species $Cd_3A_8H_7$, $Cd_3A_8H_5$, and $CdA_4H_2$ only as tentative values. Even though the removal of these species from the equilibrium model increased the value of $\sigma$ around 0.2, which is significant, the standard deviation of their formation constants is high and the correlation between the theoretical and experimental curves in the corresponding range is not very good, as can be seen in Figure 4.

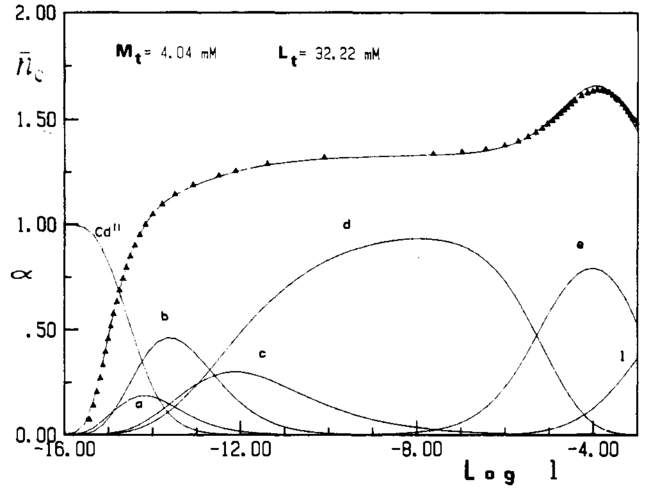

**Figure 7.** Distribution of species curves together with the variation of the average number of completely deprotonated ligands bound per Cd(II), $\bar{n}_c$, as a function of the calculated concentration of free completely deprotonated ligand, $l$. For the key to the symbols, see Table IV.

The distribution-of-species curve together with the corresponding $\bar{n}_c$ vs log $l$ curve is given in Figure 7. In agreement with previous results[21] the maximum of the $\bar{n}_c$ vs log $l$ curve coincides with the presence in solution of the species with the highest $r/p$ ratio, $Cd(HA)_4$, the subsequent decrease being due to the deprotonation of this species without changing the number of bound ligands. Such an interpretation agrees with that made in the Cd(II)–MEA system,[14] when MEA = 2-amino-1-ethanethiol.

**Comparison of the Systems Cd(II)–MMA, Cd(II)–4MP, and Cd(II)–MPA.** As a first step for a systematic study of the soluble species formed in Cd(II)–aliphatic $\gamma$-mercapto amine systems the ligands MMA, 4-MP, and MPA seem to be a good choice. Thus, while MMA and MPA differ exclusively in the degree of substitution on the amine group, the difference between MMA and 4-MP lies in the flexibility of the hydrocarbon chain linking the two functional groups. The stoichiometry of the cadmium complex species existing in solution up to pH ≈ 9 as well as the corresponding formation constants for the three ligands are given in Table V. These data clearly indicate that MMA and 4-MP behave very similarly as the same complex species are formed, the only difference being the greater stability of Cd(II)–MMA complexes. Assuming that the mechanism of formation and geometry of the species proposed for the Cd(II)–4MP system[20b] are also valid for Cd(II)–MMA solutions, the greater solubility of the latter complexes can be rationalized, as the predominance of $Cd_3(HA)_8$ species over $Cd_3(HA)_6$ and $Cd_4(HA)_9$ complexes (Figure 6A), which have been considered as the precursors of polymeric chains, makes solid formation more difficult. The structure of the solid complex $[Cd(4\text{-}MP)_2](ClO_4)_2$,[18a] which was detected in potentiometric solutions for the first time, supports the previous argument.

Soluble cadmium species with MPA in its monoprotonated form do not coincide with the corresponding species found with MMA and 4-MP ligands (Table V). Despite that, this difference is perfectly compatible with previous assumptions made relative to the geometry of the complexes and their mechanism of formation. Species of formula $Cd_3(HA)_6$, $Cd_4(HA)_8$, and $Cd_4(HA)_9$ (see

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[29] (a) Vives, J. Ph.D. Thesis, Departament de Química, Universitat Autònoma de Barcelona, Barcelona, Spain, 1987. (b) For a detailed discussion on IR spectra of M(II)–MMA (M = Ni, Pd) complexes with different structures see ref 19a.

[30] The synthesis and structural characterization of several cadmium complexes of 4-MP, MMA, and MPA will be the object of a future publication.

Table V for ligand identification) can be the precursors of polymeric chains of formula $[Cd(HA)_2]_n^{2n+}$ while the complexes $Cd_3(HA)_8$, $Cd_4(HA)_{10}$, and $Cd_5(HA)_{12}$, the last one analogous to $[Zn_5(4\text{-}MP)_{12}]^{10+}$,[19a] can be considered as the longest soluble fragments of a infinite polymeric chain, under our experimental conditions.

The IR spectra of solid cadmium complexes with the three ligands in their completely deprotonated form, $[Cd(MMA)_2]$, $[Cd(4\text{-}MP)_2]$,[29,30] and $[Cd_3(MPA)_4](ClO_4)_2{\cdot}H_2O$,[31] show that only in the last case does chelation occur, which agrees well with the structural differences of the ligands. The chelating ability of MPA, although in solutions containing Cd(II) it is lower than that of MEA,[14,21] is the greatest among the γ-mercapto amines we have studied. A good example of this different behavior is provided by nickel complexes, where chelates of the same stoichiometry as those found with MEA[32] are formed with MPA[33] but coordination occurs only through sulfur if the ligands are 4-MP[18b] or MMA.[19a] The same trend has been found in the solid cadmium complexes of the four ligands.[29,31,34] If solution equilibria studies are also taken into account,[14,20,21] where chelation has been proposed only in the case of MEA and MPA, it can be proposed that, other factors being equal, in order of increasing importance, the flexibility of the hydrocarbon chain linking both functional groups, the degree of substitution on the amine function, and the length of the hydrocarbon chain determine the tendency of mercapto amines to behave as chelating agents.

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(31) Barrera, H.; Pons, J.; Suades, J. *An. Quim., Ser. B* **1984**, *80*, 311.

(32) Wei, C. H.; Dahl, L. F. *Inorg. Chem.* **1970**, *9*, 1878.

(33) Barrera, H.; Suades, J.; Perucaud, M. C.; Brianső, J. L. *Polyhedron* **1984**, *3*, 839.

(34) Jicha, D. C.; Busch, D. H. *Inorg. Chem.* **1962**, *1*, 872.

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# Does One-Electron Transfer to Nickel(II) Porphyrins Involve the Metal or the Porphyrin Ligand?

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Nickel("I") complexes can be reversibly produced by one-electron electrochemical reduction of nickel(II) porphyrins within the time scale of cyclic voltammetry as well as thin-layer and conventional cell electrolysis in solvents such as dimethylformamide and benzonitrile. UV-vis and ESR spectroscopies indicate the formation of a nickel(I) complex rather than the anion radical of the nickel(II) porphyrin. ESR data suggest an out-of-plane displacement of the nickel(I) ion caused by the insufficient size of the hole offered by the porphyrin ligand.

Nickel(I) macrocyclic complexes have attracted active attention during the last 10 years as powerful catalysts of the electrochemical reduction of electrophiles. The principle of the reaction consists in generating electrochemically the Ni(I) complex from the Ni(II) complex. The former then reacts with the electrophile, regenerating the latter. Main applications have concerned the reduction of alkyl halides[2,3] and of carbon dioxide.[4]

Another source of interest for nickel(I)-tetraazamacrocyclic complexes relates to coenzyme F430, an hydrocorphinoid nickel(II) complex involved in the reductive cleavage of *S*-methyl coenzyme M ((methylthio)ethanesulfonate) to coenzyme M (mercaptoethanesulfonate) and methane.[5] Recent findings point to the involvement of the corresponding Ni(I) complex in this reaction as indicated by the similarity of the ESR signal detected in whole cells of *Methanobacterium thermoautotrophicum*[6a] and of the ESR spectrum of the reduced form of the pentamethyl ester of coenzyme F430.[6b]

In both cases, the ability of the starting nickel(II) complex to form, upon one-electron transfer, a nickel(I) complex rather than the anion radical of the macrocyclic ligand appears as a key point for obtaining an efficient catalysis. In the latter case, one indeed expects the formation of ring coupling products that would eventually stop the propagation of the catalytic reaction. Moreover, nickel(I) complexes are expected to react with electrophiles, halogen, or halonium donors by transfer of their unpaired electron in an inner-sphere manner, being thus more efficient and more specific than ring anion radicals, which are likely to function as outer-sphere electron donors.[7,8] In this connection, ESR and UV-vis spectroscopy are useful tools to assess the relative importance of the Ni(I) and Ni(II) anion radical resonant forms. The electrochemical and ESR study of an extended series of nickel-tetraazamacrocyclic complexes involving neutral ligands[9a] has shown that Ni(I) is obtained with saturated macrocycles and with macrocycles containing isolated imine groups whereas an

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(1) (a) Universitê de Paris 7. (b) Unitê Inserm 219.

(2) (a) Gosden, C.; Healy, K. P.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1978**, 972. (b) Healy, K. P.; Pletcher, D. *J. Organomet. Chem.* **1978**, *161*, 109. (c) Gosden, C.; Pletcher, D. *J. Organomet. Chem.* **1980**, *186*, 401. (d) Becker, J. Y.; Kerr, J. B.; Pletcher, D.; Rosas, R. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *117*, 87. (e) Gosden, C.; Kerr, J. B.; Pletcher, D.; Rosas, R. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *117*, 101.

(3) (a) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 713. (b) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 719. (c) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 5353. (d) Ram, M. S.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 3267.

(4) (a) See ref 4b and references cited therein. (b) Beley, M.; Collin, J. P.; Ruppert, R.; Sauvage, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 7461.

(5) (a) Gunsalus, R. P.; Wolfe, R. S. *FEMS Microbiol. Lett.* **1978**, *3*, 191. (b) Dickert, G.; Klee, B.; Thauer, R. K. *Arch. Microbiol.* **1980**, *124*, 103. (c) Whitman, W. B.; Wolfe, R. S. *Biochem. Biophys. Res. Commun.* **1980**, *92*, 1196.

(6) (a) Albract, S. P. J.; Ankel-Fuks, D.; Van der Zwann, J. W.; Fontjin, R.; Thauer, R. K. *Biochem. Biophys. Acta* **1986**, *870*, 50. (b) Jaun, B.; Pfaltz, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1327.

(7) (a) For a recent discussion of this point, see ref 7b. (b) Lexa, D.; Savêant, J. M.; Su, K. B.; Wang, D. L., in press.

(8) The mechanism of the reaction with alkyl halides was first deemed to involve an $S_N2$ attack of the Ni(I) nucleophile on the carbon center.[2] However more recent studied concluded the likeliness of an halogen atom transfer mechanism based on the observed acceleration of the reaction when passing from methyl to primary and secondary halides.[3]