Airy functions.[55] The results we have obtained are reported in Table I: of course these figures are significant only with regard to their order of magnitude because of the inherent approximations.[53] However, we note that the conversion rate for $\Delta Q = 0.1$ Å is very high at any temperature and faster or of the order of nuclear motion (10^{12}–10^{13} s^{-1}) so that only electronic and, perhaps, vibrational spectroscopies could "catch" molecules in a pure spin state. Instead, the conversion rates are strongly reduced at low temperature when $\Delta Q = 0.2$ Å, and consequently, even "slower" spectroscopies, like Mössbauer spectroscopy (precession time of the ^{57}Fe nucleus in the range 10^{-7}–10^{-9} s), are suitable to detect spin isomers simultaneously.

At this point it is important to remember that the previous conversion rates were obtained by considering the overall process $^1A_1 \rightarrow {}^3E$, as it was shown in ref 53. A more accurate treatment should take into account two different conversion processes: (i) $\Gamma_1(^1A_1) \rightarrow \Gamma_1(^3E)$, for which rates very similar to those reported in Table I are evaluated; (ii) $\Gamma_1(^1A_1) \rightarrow \Gamma_{2-5}(^3E)$, which is at least 2 orders of magnitude slower than the previous one, because only small perturbing terms, like low-symmetry fields or strain, can couple $\Gamma_1(^1A_1)$ with the other components of the triplet.

To conclude, when the coupling between the potential wells of the pure spin states and the energy difference between the minima are sufficiently small, solid-state effects can stabilize one or both species in the lattice.[19] Instead, in the presence of a strong coupling, it does not make sense to discuss the simultaneous presence of different chromophores in the lattice, because spin–orbit coupling washes out the two wells.

The important point is what we can "see" by means of our experiments or, in other words, whether the characteristic time of our measurements is short enough to individuate pure spin states. Actually, some singlet–triplet spin equilibria in iron(II) complexes appear to be typical examples of type a systems. In these compounds, a strong coupling should be effective and a situation like that depicted in Figure 1b or 2b should occur. Consequently, with the experiments that have been performed so far[6,11,12,49] (except, perhaps, electronic spectroscopy[11]), their fast conversion rate prevents the identifying of pure spin states.

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Thermodynamics of Complexation of Lanthanide Ions by *N*-Methylethylenediamine-*N*,*N'*,*N'*-triacetic Acid

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The thermodynamic parameters of complexation of lanthanide cations with *N*-methylethylenediamine-*N*,*N'*,*N'*-triacetate ion (MEDTA) were determined by potentiometric and calorimetric techniques. The measurements were conducted at 25 °C and ionic strength of 0.10 and 0.50 M (NaClO$_4$). The observed decrease in stability as well as in enthalpy values of Ln–MEDTA chelates compared to EDTA species is attributed to a weaker Ln–N interaction due to the presence of a single acetate arm associated with one of the nitrogens.

Introduction

Amino polycarboxylic acids form strong chelates with the trivalent lanthanide metals. Several of these ligands have been used as reagents for the analytical assay of the lanthanides and for their separation by ion exchange. The thermodynamics and kinetics of chelation of many of these lanthanide–ligand systems have been measured. Of interest in this paper are the complexes of the lanthanides with *N*-methylethylenediamine-*N*,*N'*,*N'*-triacetic acid (MEDTA). Powell et al.[1] reported the stability constants for LnMEDTA complexation. The dissociation kinetics of these chelates were also described recently.[2] Qualitative information on the structure of LnMEDTA in solution was obtained by ^{1}H NMR studies, which confirmed pentadentate chelation.[3]

MEDTA is interesting as a ligand of intermediate chelation between, for example, iminodiacetic acid (IDA) and ethylenediaminetetraacetic acid (EDTA). To allow comparisons with such ligands, we have determined the thermodynamic parameters of complexation of lanthanides by MEDTA.

Experimental Section

Reagents. Lanthanide perchlorate solutions were prepared and standardized as described previously.[4] A pure, recrystallized sample of MEDTA in the acid form was prepared as reported elsewhere.[2,5]

Potentiometry. The protonation constants of MEDTA and the stability constants of the LnMEDTA complexes were determined in a solution of 0.50 M (NaClO$_4$) ionic strength. The potentiometric measurements were made with a pH-meter (Corning 130) fitted with a combination glass–calomel electrode. The electrode was calibrated with standard "BuffAR" of pH 4.01 and 7.00. In basic media, borax solution (0.01 M) served as a standard buffer of pH 9.17. Corrections for the hydrogen ion activity in solutions of 0.10 and 0.50 M ionic strength were obtained by using the activity coefficients 0.782 and 1.585, respectively.[6,7] The p*K* values for the free ligand were calculated by minimizing the residuals in $\bar{n}_H$ for a series of measurements in the appropriate buffer region. The values of the stability constants were obtained by titrating volumes of equimolar amounts of metal and ligand with standard 0.10 M (CO$_2$-free) sodium hydroxide solution. In all measurements, the ligand concentration was kept at 0.001 M, the temperature was maintained at 25 °C, and the ionic strength of the reaction medium was maintained constant by the addition of the appropriate amount of sodium perchlorate solution.

The data were processed by using the BETA program based on the SIMPLEX algorithm and written in this laboratory by Dr. William Cacheris. The uncertainties in these constants were estimated from the curvature of the sum square residuals with respect to each parameter. Different models were used in the potentiometric data analysis, i.e. formation of LnMEDTA only and formation of LnMEDTA plus LnHMEDTA$^+$. The value of β_{111} (β_{111} = [LnHMEDTA$^+$]/[Ln^{3+}][H$^+$][MEDTA^{3-}]) for the second model was unrealistic (β_{111} = 2 ± 57000) and the $\bar{n}_H$ values for this model were also unacceptable ($<10^{-6}$). The conclusion was that formation of LnHMEDTA$^+$ was not significant under these concentrations and pH conditions.

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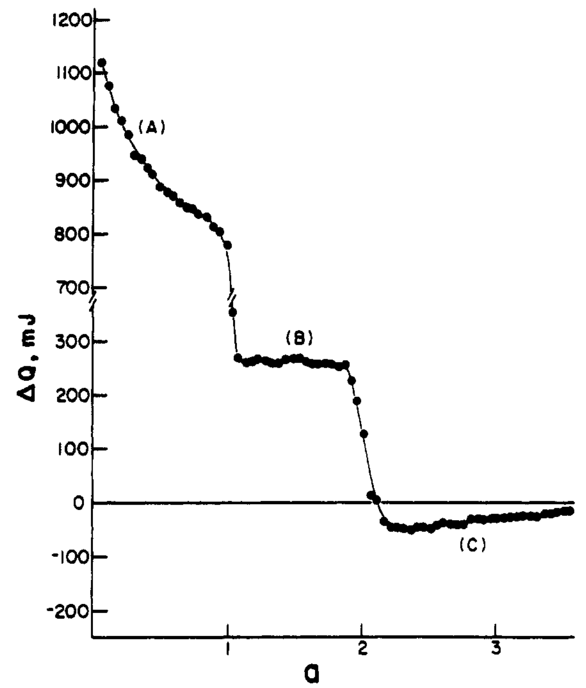

Figure 1. Calorimetric titration curve of the trisodium salt of MEDTA (0.508 mmol) with 0.1 M perchloric acid. *a* is the moles of acid added per mole of ligand, $I = 0.10$ M ($NaClO_4$); $T = 298$ K.

Table I. Thermodynamic Values for Protonation of MEDTA

reaction	log K^a	$-\Delta H_n$, kJ mol^{-1}	ΔS_n, J K^{-1} mol^{-1}	I, M
$H^+ + L^{3-} \rightleftharpoons HL^{2-}$	10.31 ± 0.005	31.24 ± 0.10	93 ± 1	0.10
	10.19 ± 0.04	36.10 ± 0.80	74 ± 3	0.50
$H^+ + HL^{2-} \rightleftharpoons H_2L^-$	5.42 ± 0.01	10.92 ± 0.05	67 ± 1	0.10
	5.55 ± 0.02	13.50 ± 0.78	61 ± 3	0.50
$H^+ + H_2L^- \rightleftharpoons H_3L^0$	2.45 ± 0.035	-2.61 ± 0.30	56 ± 1	0.10
	2.40 ± 0.01	-2.76 ± 0.05	55 ± 1	0.50
$H^+ + H_3L^0 \rightleftharpoons H_4L^+$	1.93 ± 0.065	-1.79 ± 0.30	43 ± 1	0.10
	1.72 ± 0.02	-2.90 ± 0.10	43 ± 1	0.50

[a] The values for 0.10 M ionic strength are from ref 1 while those for 0.50 M were determined in the present study.

Calorimetry. Calorimetric measurements were conducted with an adiabatic calorimeter[8] interfaced with an Ohio Scientific computer,[9] following the general procedure used in this laboratory.[10] The heats of complexation were obtained by titrating the ligand solution adjusted to pH ~6 into the metal solution adjusted to a pH value between 5 and 6. For these experimental conditions, reaction 1 was dominant. All measurements were carried out at 25 °C, and the ionic strength of each solution was adjusted to the proper value with sodium perchlorate as the background electrolyte. Because of the limited amount of ligand available, only the protonation enthalpy and several metal complexation enthalpy measurements were duplicated. The uncertainties reported are the deviations from the average of each individual point of the titration curve(s). The complexation enthalpies were determined in solutions of 0.10 M and 0.50 M ($NaClO_4$) ionic strength.

$$Ln^{3+} + HMEDTA^{2-} \rightleftharpoons LnMEDTA + H^+ \qquad (1)$$

Results and Discussion

Figure 1 is a plot of the protonation enthalpy measurements. These calorimetric titrations showed the three buffer regions labeled A, B, and C in the graph. In region A, the excess base and $MEDTA^{3-}$ (to $HMEDTA^{2-}$) are being protonated. In region B, formation of H_2MEDTA^- occurs. $HMEDTA^{2-}$ and H_2MEDTA^- are protonated at nitrogen. In region C, H_3MEDTA and H_4MEDTA^+ are formed by protonation of carboxylate groups. Table I lists the $pK_{a(n)}$ values reported in ref 1 for 0.10 M ionic strength and those at 0.50 M from this study. Also given in the table are the values of ΔH and ΔS at 0.10 and 0.50 M ionic strength as determined in this work.

Table II. Potentiometric Titration Data For Eu-MEDTA ($I = 0.50$ M ($NaClO_4$); $T = 298$ K)[a]

$V_{titrant}$, mL	$10^4[H^+]_{obsd}$, M	$10^4[H^+]_{calcd}$, M	$10^4[Eu^{3+}]$, M	$10^{13}[L^{3-}]$, M	$\bar{n}$
0.10	13.122	13.154	9.363	0.747	0.223
0.20	11.995	12.035	8.998	0.876	0.252
0.30	10.965	10.976	8.603	1.028	0.283
0.40	9.931	9.973	8.181	1.209	0.317
0.50	9.016	9.023	7.730	1.423	0.353
0.60	8.110	8.123	7.254	1.679	0.392
0.65	7.709	7.691	7.006	1.826	0.412
0.70	7.311	7.269	6.752	1.988	0.433
0.75	6.902	6.858	6.492	2.168	0.454
0.80	6.501	6.457	6.227	2.366	0.476
0.85	6.109	6.066	5.956	2.588	0.498
0.90	5.728	5.683	5.679	2.835	0.521
0.95	5.370	5.310	5.397	3.114	0.544
1.00	5.000	4.945	5.110	3.429	0.568
1.05	4.645	4.589	4.818	3.788	0.592
1.10	4.295	4.239	4.522	4.201	0.617
1.15	3.945	3.897	4.220	4.680	0.642
1.20	3.598	3.562	3.915	5.242	0.668
1.25	3.266	3.234	3.604	5.909	0.694
1.30	2.944	2.912	3.290	6.713	0.720
1.35	2.618	2.595	2.972	7.702	0.747
1.40	2.301	2.285	2.649	8.946	0.774
1.45	1.991	1.980	2.323	10.557	0.802
1.50	1.679	1.680	1.993	12.723	0.830
1.55	1.352	1.384	1.659	15.791	0.858
1.60	1.064	1.094	1.321	20.467	0.887

[a] Experimental conditions: cup solution, $C_L = 1.2168$ mM, $C_M = 1.2069$ mM, $C_H = 3.6504$ mM, $V = 50.0$ mL; titrant, $C_{NaOH} = 0.1014$ M; calculated constant, log $\beta_{101} = 12.59 \pm 0.01$.

Table III. Calorimetric Titration Data for Ho-MEDTA ($I = 0.50$ M ($NaClO_4$); $T = 298$ K)[a]

$V_{titrant}$, mL	$-\Sigma Q_{obsd}$, mJ	$\bar{n}$	10^2[ML], mmol	$-\Delta H_{101}$, kJ mol^{-1}
0.50	116	0.038	0.491	11.44
1.00	232	0.050	0.979	11.37
1.50	348	0.062	1.463	11.18
2.00	459	0.074	1.942	11.29
2.50	564	0.086	2.415	11.50
3.00	666	0.098	2.883	11.69
3.50	781	0.110	3.344	11.34
4.00	885	0.121	3.797	11.30
4.50	983	0.133	4.244	11.35
5.00	1076	0.144	4.683	11.44
5.50	1172	0.155	5.115	11.40
6.00	1259	0.166	5.540	11.48
6.50	1342	0.176	5.957	11.57

[a] Experimental conditions: cup solution, $C_M = 7.227$ mM, $C_L = 0.194$ mM, $C_H = 0.189$ mM, $V = 50.0$ mL; titrant, $C_L = 9.875$ mM, $C_H = 9.626$ mM; computed enthalpy, $-\Delta H_{101} = 11.38 \pm 0.30$ kJ mol^{-1}.

Tables II and III are sets of typical potentiometric and calorimetric titration data, respectively. The stability constants, β_{101}, and the corresponding thermodynamic values of complexation are given for 0.10 ($NaClO_4$) and 0.50 M ($NaClO_4$) ionic strengths in Table IV. These values refer to reaction 2. In order to use the stability constants of ref 1 for the 0.10 M ($NaClO_4$) ionic strength system, the values had to be corrected for $LnNO_3^{2+}$ formation in the 0.10 M (KNO_3) solution used as the inert electrolyte. The "corrected" values listed in Table IV were calculated from the experimental stability constants of ref 1 by

$$Ln^{3+} + MEDTA^{3-} \rightleftharpoons LnMEDTA \qquad (2)$$

$$\beta_{101}^{cor} = \beta_{101}^{exptl}(1 + \beta'[NO_3^-]) \qquad (3)$$

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Table IV. Thermodynamic Parameters of the Complexation of Lanthanides with MEDTA

metal	log β_{101}[a]	$-\Delta G_{101}$, kJ mol^{-1}	$-\Delta H_{101}$, kJ mol^{-1}	ΔS_{101}, J K^{-1} mol^{-1}
A. I = 0.10 M (NaClO$_4$); T = 298 K				
La	11.58 ± 0.01	66.07 ± 0.06	5.32 ± 1.86	204 ± 6
Pr	12.45 ± 0.01	71.03 ± 0.06	6.80 ± 1.44	216 ± 5
Nd	12.64 ± 0.02	72.12 ± 0.11	9.35 ± 0.28	211 ± 1
Sm	13.00 ± 0.02	74.17 ± 0.11	8.96 ± 0.21	219 ± 1
Eu	13.08 ± 0.02	74.63 ± 0.11	5.80 ± 0.24	231 ± 1
Gd	13.07 ± 0.03	74.57 ± 0.17	4.29 ± 0.14	236 ± 1
Tb	13.42 ± 0.03	76.57 ± 0.17	5.02 ± 0.09	240 ± 1
Dy	13.67 ± 0.02	77.99 ± 0.11	5.67 ± 0.17	243 ± 1
Ho	13.86 ± 0.01	79.08 ± 0.06	6.35 ± 0.18	244 ± 1
Er	14.08 ± 0.01	80.33 ± 0.06	6.79 ± 0.18	247 ± 1
Tm	14.35 ± 0.01	81.87 ± 0.06	6.87 ± 0.16	252 ± 1
Yb	14.46 ± 0.01	82.50 ± 0.06	9.36 ± 0.13	245 ± 1
Lu	14.54 ± 0.02	82.96 ± 0.11	7.99 ± 0.07	252 ± 1
Y	13.42 ± 0.01	76.57 ± 0.06	3.44 ± 0.09	245 ± 1
B. I = 0.50 M (NaClO$_4$); T = 298 K				
La	11.08 ± 0.02	63.22 ± 0.11	12.60 ± 0.35	170 ± 1
Pr	11.89 ± 0.02	67.84 ± 0.11	15.72 ± 0.28	175 ± 1
Nd	12.14 ± 0.03	69.27 ± 0.17	16.36 ± 0.21	178 ± 1
Sm	12.42 ± 0.05	70.86 ± 0.29	14.09 ± 0.55	191 ± 2
Eu	12.59 ± 0.03	71.83 ± 0.17	13.19 ± 0.40	197 ± 1
Gd	12.63 ± 0.02	72.06 ± 0.11	11.33 ± 0.36	204 ± 1
Tb	12.93 ± 0.04	73.77 ± 0.23	10.12 ± 0.51	214 ± 2
Dy	13.17 ± 0.03	75.14 ± 0.17	11.57 ± 0.59	213 ± 2
Ho	13.37 ± 0.03	76.28 ± 0.17	11.38 ± 0.30	218 ± 1
Er	13.53 ± 0.05	77.20 ± 0.29	12.81 ± 0.32	216 ± 1
Tm	13.74 ± 0.05	78.39 ± 0.29	13.92 ± 0.48	216 ± 2
Yb	14.01 ± 0.02	79.94 ± 0.11	15.05 ± 0.73	218 ± 2
Lu	14.18 ± 0.02	80.91 ± 0.11	16.27 ± 0.37	217 ± 1
Y	12.89 ± 0.02	73.54 ± 0.11	10.15 ± 0.20	213 ± 1

[a] The log β_{101} values for 0.10 M ionic strength are from ref 1 and are corrected from KNO$_3$ medium to NaClO$_4$.

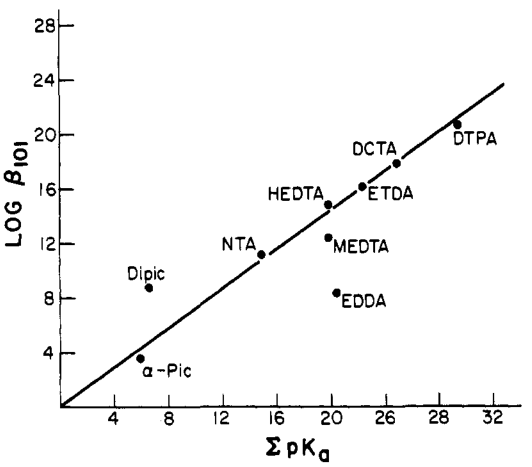

Figure 2. Correlation of log β_{101} of the Sm(III) complexes and $\sum pK_a$ of the ligands (I = 0.50 M).

where [NO$_3^-$] = 0.10 M and β', the stability constants for LnNO$_3^+$ formation, were taken from ref 11. The error limits in log β_{101}, ΔG_{101} and ΔS_{101} were compounded to include the uncertainty in the β' values.

Figure 2 shows the correlation of the log β_{101} and the p$K_{a(n)}$ values for Sm(III) with a number of amino polycarboxylic acid ligands (the pK_a values were obtained from ref 12 and 13). Sm(III) was used for this comparison as it represents the "average" behavior. Also, Sm(III) has more literature values that could be used for the comparisons of Figures 2 and 3. The correlation in Figure 2 has been noted for many metal–ligand systems and reflects the strongly ionic nature of the bonding of the complex. Structural effects can perturb the correlation as in the case of the dipicolinate complex. The extra stabilization (log β_{101} is above the "normal" line) of the Sm–dipicolinate complex was attributed to the rigidity of the aromatic ring, which results in a shorter Ln–N distance than would be present in complexes with the more flexible alkyl ligands.[13,14] For Sm–ethylenediamine-*N*,*N'*-diacetate (Sm–EDDA) complex, each nitrogen is involved in a single O–Ln–N ring in contrast to the double-ring system for each nitrogen in EDTA. This would lead to a weakened Ln–N interaction and decreased value of log β_{101} as the average Ln–N distance should be greater in EDDA than in EDTA. Similarly, the binding of Sm(III) to the nitrogen in MEDTA associated with a single carboxylate group should have a smaller contribution to the complex stability. Since only one Sm–N bond is weakened in MEDTA, the decreased stability is less than that in the EDDA complex where both Sm–N interactions are weaker.

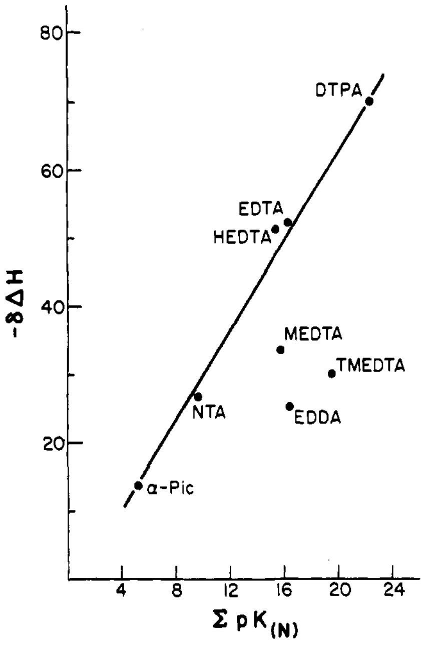

Figure 3. Relation between the residual enthalpy ($\delta(\Delta H) = \Delta H_{101} - 6.5n$) and the total basicity of the nitrogen donor atoms of the ligands.

The previous nmr study[3] had shown that the Ln–N bond lifetime associated with the single carboxylate group was shorter than that of the Ln–N bonds in the EDTA complex. By contrast, the Ln–N bond of the double carboxylate end of the MEDTA has a longer lifetime than the Ln–N bonds in LnEDTA.

The entropy of complexation is, within error limits, the same value as that reported for the NTA and HEDTA complexes. All three ligands have three carboxylate groups while NTA has a single nitrogen donor and HEDTA and MEDTA have two nitrogen donor atoms. This agreement in entropy is consistent with the proposal in ref 14 that the lanthanide–carboxylate interactions alone can account for the entropy changes. Not only was a linear trend observed in ref 14 between the ΔS of 1:1 complexation and the number of carboxylate groups in the ligand (irrespective of the number of nitrogen donor sites) but the ΔS value was equal to $n\Delta S_{Ac}$, where n = number of carboxylates and ΔS_{Ac} = entropy of (Sm–acetate)$^{2+}$ formation at the same ionic strength. This suggested[14] that the portion on the enthalpy of complexation due to metal–carboxylate interaction could also be given by $n\Delta H_{Ac}$ ($\Delta H_{Ac} \simeq$ 6.5 kJ mol^{-1}). The value of $\delta(\Delta H)$, as defined by

$$\delta(\Delta H) = \Delta H_{101} - n(\Delta H_{Ac})$$

should be a measure of the metal–nitrogen donor interactions. The

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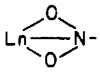
satisfactory correlation of $\delta(\Delta H)$ with $\sum pK_{a(N)}$, the sum of the pK_a values for the nitrogen donor sites of the ligand, for the series of Sm–amino polycarboxylate complexes provided support for such an analysis. A similar treatment has been used for interpretation of the thermodynamic data on 1:1 complexation of lanthanides with 1,4-dinitrilobutane-*N,N,N′,N′*-tetraacetate (TMEDTA).[7]

The plot of $-\delta(\Delta H_N)$ vs. $\sum pK_{a(N)}$ in Figure 3 shows that EDDA, MEDTA, and TMEDTA do not correlate with other complexes. In TMEDTA, the explanation offered[7] was that the 7-membered $\overline{\text{N–Ln–N}}$ chelate ring is much less stable than the 5-membered ring of LnEDTA. Consequently, the Ln–N interaction is weakened. Also, interaction with a nitrogen donor apparently is weakened when a single carboxylate group is associated with that nitrogen donor as there is only one $\overline{\text{O–Ln–N}}$ chelate ring compared to two such rings



in Ln–EDTA, etc. In Sm–MEDTA, only one of the nitrogen donor interactions is so "weakened", whereas in Sm–EDDA, both Sm–N interactions are affected, which is consistent with the data in Figure 3.

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Successful Photocatalytic Reduction of MV^{2+} with $[Cu(NN)(PPh_3)_2]^+$ (NN = 2,9-Dimethyl-1,10-phenanthroline or 4,4′,6,6′-Tetramethyl-2,2′-bipyridine) upon Near-UV-Light Irradiation and a Novel Solvent Effect on Its Catalytic Activity

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Methylviologen (MV^{2+}) is photocatalytically reduced by Cu(I) complexes $[Cu(NN)(PPh_3)_2]^+$ (NN = 2,9-dimethyl-1,10-phenanthroline or 4,4′,6,6′-tetramethyl-2,2′-bipyridine) in an alcohol–water mixed solvent. The quantum yields for the MV^{2+} reduction decrease in the order NN = 2,9-dimethyl-1,10-phenanthroline > 4,4′,6,6′-tetramethyl-2,2′-bipyridine >> 4,4′-dimethyl-2,2′-bipyridine > 1,10-phenanthroline, whereas the 2,2′-bipyridine and 4,7-diphenyl-1,10-phenanthroline analogues hardly reduce MV^{2+} at all. In this catalytic reaction, alcohol reduces the oxidized $[Cu^{II}(NN)(PPh_3)_2]^{2+}$ so as to complete the catalytic cycle. A reasonable reaction mechanism is deduced, which is supported by a kinetic study; the Cu(I) complex absorbs near-UV light to generate its photoexcited state, followed by the formation of the encounter complex with MV^{2+} and then an electron transfer from the Cu(I) complex to MV^{2+}. An interesting solvent effect is found in the present catalytic system, which is also examined by kinetic treatment; when the water content in the solvent is increased, the lifetime of the photoexcited Cu(I) complex becomes longer, and as a result, the catalytic activity of the Cu(I) complex becomes higher.

Introduction

In the last 10 years, many attempts have been made to find photocatalytic systems capable of reducing H^+ or MV^{2+} (methylviologen),[1] and several catalytic systems have hitherto been reported; for example, $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine),[2] Zn–porphyrin, and Ru–porphyrin complexes[3] catalytically reduce MV^{2+} upon visible-light irradiation, yielding H_2 gas in the presence of Pt–colloid. Also, $[CuCl_3]^{2-}$ can reduce H^+ stoichiometrically upon UV-light irradiation.[4] Nevertheless, there are only a few investigations on photoreduction catalysis of Cu(I) complexes, whereas Cu(I) complexes with bpy, 1,10-phenanthroline (phen), or their derivatives have the metal-to-ligand charge-transfer (MLCT) excited state as the lowest excited state,[5] similar to $[Ru(bpy)_3]^{2+}$. To our knowledge, two examples of photocatalytic reduction by Cu(I) complexes have been reported quite recently: the catalytic reduction of Co(III) complexes by $[Cu(dmp)(PPh_3)_2]^+$, (dmp = 2,9-dimethyl-1,10-phenanthroline)[6] and the catalytic reduction of H^+ (i.e., H_2 gas evolution) by $[Cu(dmp)_2]^+$ and $[Cu(2,9\text{-dpp})_2]^+$ (2,9-dpp = 2,9-diphenyl-1,10-phenanthroline) in the presence of MV^{2+} and its derivative.[7]

In this work, the effective photocatalytic reduction of MV^{2+} has been carried out with $[Cu(NN)(PPh_3)_2]^+$ (NN = bpy, phen, and their derivatives) in an alcohol–water mixed solvent upon

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