3786 *Inorg. Chem.* **1988**, *27*, 3786–3789

Contribution from the Department of Chemistry, University of Texas at El Paso, El Paso, Texas 79968-0513,
Contrast Media Research Department, Squibb Institute for Medical Research, New Brunswick, New Jersey 08903-0191,
and Institute of Organic Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44, 01-224 Warszawa, Poland

Equilibria and Dissociation Kinetics of Lanthanide Complexes of Diaza Crown Ether Carboxylic Acids

C. Allen Chang,[*,†] Peter H.-L. Chang,[†] V. K. Manchanda,[†] and S. P. Kasprzyk[‡]

Received May 27, 1987

The equilibria and dissociation kinetics of lanthanide and several transition-metal and Pb(II) complexes of some diaza crown ether carboxylic acids are studied. The ligands are K22MA (1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N*-acetic acid), K22DP (1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N*,*N*′-di-β-propionic acid), and K22MP (1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N*-β-propionic acid). The protonation constants of these ligands are similar to those of the structural analogues and are in the range $\log K_1 = 8.80$–9.01 and $\log K_2 = 7.26$–8.16. The stability constants are all lower than that of their structural analogue K22DA (1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N*,*N*′-diacetic acid) due to the reduction of the chelate effect or an unfavorable steric effect or both. The kinetic dissociation rates are all faster as compared to those of K22DA complexes. Acid-dependent (k_H) and acid-independent (k_d) rate constants are obtained by the measurement of rates at various pH values, and they correlate inversely with the values of stability constants.

Our recent studies on the chemistry of lanthanide complexes of macrocyclic ligands with ionizable pendant functional groups have led to a better understanding of their stereochemical and coordination properties. Two ionizable macrocyclic ligands, i.e. 1,7-diaza-4,7,13-trioxacyclopentadecane-*N*,*N*′-diacetic acid (dapda or K21DA) and 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N*,*N*′-diacetic acid (dacda or K22DA), are prepared for most explorative work such as complex formation stability,[1,2] dissociation kinetics,[3-5] ternary complex formation,[6] and applications in solvent extraction.[7-9] The choice of the two ligands is based upon the fact that they possess two of the most important ion-binding characteristics, i.e. charge and size. It is hoped that if the concept of stereochemical constraint is also built into the ligand design, a selective reagent may result.

In order to extend the understanding of these systems, we have performed additional studies on the thermodynamic and kinetic stabilities of lanthanide complexes of carboxylic acid derivatives of diaza-18-crown-6 (K22) other than K22DA. Three ligands, i.e. K22MA, K22MP, and K22DP, are of interest, and their structural formulas are shown in Figure 1. The results are reported in this paper.

Experimental Section

A. Synthesis of Ligands. All ligands were synthesized according to methods described below. Elemental analyses were performed at the Institute of Organic Chemistry, Polish Academy of Sciences, by standard procedures.

1. 1,10-Diaza-4,7,13,16-tetraoxacyclooctadecane-*N*-acetic Acid Hydrate (K22MA·H_2O). A solution of 10 mmol of chloroacetic acid in 25 mL of water was adjusted to pH 9.5 by using a 4 M NaOH solution. This solution was added dropwise over a period of 4 h to a boiling solution of 15 mmol of K22 (50% excess) in 20 mL of water. The mixture was refluxed for 10 h, and then it was adjusted to pH 12 by using 4 M NaOH. The solution was extracted with chloroform (3 × 50 mL) to remove any unreacted K22. The aqueous layer was concentrated in vacuo over P_4O_{10} and purified by passing through an ion-exchange column (Amberlite IR-120). The product was recrystallized from ethanol; yield 70%. Anal. Calcd for $C_{14}H_{28}N_2O_6{\cdot}H_2O$: C, 49.70; H, 8.88; N, 8.28. Found: C, 49.45; H, 8.86; N, 8.28.

2. 1,10-Diaza-4,7,13,16-tetraoxacyclooctadecane-*N*-β-propionic Acid Hydrate (K22MP·H_2O). This ligand was prepared according to the method for K22MA by using K22 and β-bromopropionic acid. Anal. Calcd for $C_{15}H_{30}N_2O_6{\cdot}H_2O$: C, 51.13; H, 9.09; N, 7.95. Found: C, 51.50, H, 9.44; N, 7.93.

3. 1,10-Diaza-4,7,13,16-tetraoxacyclooctadecane-*N*,*N*′-di-β-propionic Acid (K22DP). The method of Takagi et al. was used with minor modifications.[10] A mixture of 10 mmol of K22 and 50 mmol of acrylonitrile in 20 mL of absolute ethanol were refluxed for 3 h and then concentrated under reduced pressure. The residual oil was hydrolyzed with a refluxing solution of potassium hydroxide in isopropyl alcohol for 24 h. The hydrolysis mixture was neutralized with concentrated HCl, the solid KCl was removed by filtration from isopropyl alcohol solution, and the desired diacid was isolated by passing through Amberlite IR-120 cation-exchange resin and rotary evaporation. The product was recrystallized from absolute ethanol and dried in vacuo over P_4O_{10}; overall yield 60%. Anal. Calcd for $C_{18}H_{34}N_2O_8$: C, 53.19; H, 8.43; N, 6.89. Found: C, 53.11; H, 8.63; N, 6.61.

B. Preparation of Stock Solutions. Ligand solutions (0.01 M) were prepared in their fully protonated forms by adding the required amount of HCl. Tetramethylammonium hydroxide solution (0.02 M) was prepared by diluting a 20% $(CH_3)_4NOH$ methanol solution obtained from Aldrich Chemical Co. The aqueous $(CH_3)_4NOH$ solution contained a negligible amount of methanol and was standardized by using analytical reagent grade potassium hydrogen phthalate dried at 100 °C for 4 h. A 1 M solution of $(CH_3)_4NCl$ was prepared and determined by passing aliquots of the solution into a cation-exchange column in the H^+ form and by titrating the displaced H^+ ions with standard KOH solution. The standard metal salt solutions having concentrations of about 0.01 M were prepared from reagent grade nitrates (Cu^{2+}, Zn^{2+}, Pb^{2+}, Ce^{3+}, Pr^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+}), chlorides (La^{3+}, Nd^{3+}, Ni^{2+}), and sulfate (Sm^{3+}). The metal salt solutions were standardized by EDTA complexometric titrations with xylenol orange (all lanthanides), murexide (Cu^{2+} and Ni^{2+}), and eriochrome black T (Zn^{2+} and Pb^{2+}) as indicators.[11]

C. Potentiometric Titrations. All titrations were carried out at a constant ionic strength of 0.10 M $(CH_3)_4NCl$. Boiled deionized water was used for all experiments. A Fisher Model 750 Acument selective ion analyzer in conjunction with a Fisher combination electrode was employed to monitor the pH (±0.001 pH unit). The sample solutions were prepared by pipetting exact amounts of each stock solution into a titration vessel so that the final mixture was 1.0×10^{-3} M in both the ligand and the metal salt. An additional amount of standardized HCl was added into the titration mixture so that the final ligand would be in the form $H_2L{\cdot}2HCl$ (K22DP) or $HL{\cdot}2HCl$ (K22MA and K22MP). The water-jacketed titration vessel with a 50-mL capacity was purchased from Brinkmann. The vessel was always kept at 25 ± 0.1 °C by using a constant-temperature circulating bath procured from Van Waters and Rogers. Prior to each titration, the pH meter was calibrated with pH 4.00 and pH 7.00 buffer solutions (ionic strength 0.1 M). Carbonate-free

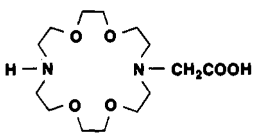
---

[*] To whom correspondence should be addressed at the Squibb Institute for Medical Research.

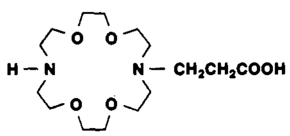
[†] University of Texas at El Paso and Squibb Institute for Medical Research.

[‡] Polish Academy of Sciences.

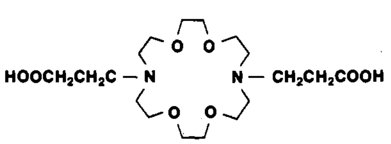
(1) Chang, C. A.; Rowland, M. E. *Inorg. Chem.* **1983**, *22*, 3866–3869.
(2) Chang, C. A.; Ochaya, V. O. *Inorg. Chem.* **1986**, *25*, 355–358.
(3) Chang, C. A.; Ochaya, V. O.; Sekhar, V. C. *J. Chem. Soc., Chem. Commun.* **1985**, 1724–1725.
(4) Sekhar, V. C.; Chang, C. A. *Inorg. Chem.* **1986**, *25*, 2061–2065.
(5) Chang, C. A.; Sekhar, V. C. *Inorg. Chem.* **1987**, *26*, 1981–1985.
(6) Chang, C. A.; Garg, B. S.; Manchanda, V. K.; Ochaya, V. O.; Sekhar, V. C. *Inorg. Chim. Acta* **1986**, *115*, 101–106.
(7) Manchanda, V. K.; Chang, C. A. *Anal. Chem.* **1986**, *58*, 2269–2275.
(8) Manchanda, V. K.; Chang, C. A. *Anal. Chem.* **1987**, *59*, 813–818.
(9) Chang, C. A.; Manchanda, V. K.; Peng, J. *Inorg. Chim. Acta* **1987**, *130*, 117–118.
(10) Takagi, M.; Ueno, K. *Chem. Lett.* **1978**, 1179–1182.
(11) Schwarzenbach, G.; Flaschka, H. *Complexometric Titrations*, 5th ed.; Methuen: London, 1969 (translated by H. M. N. H. Irving).



K22MA



K22MP



K22DP

Figure 1. Structural formulas of K22MA, K22MP, and K22DP.

$(CH_3)_4NOH$ solution was delivered from a 5-mL buret with a reading accuracy of 0.01 mL. The activity coefficient, f_{H^+}, was calculated by titrating a HCl solution of known concentration in the presence of 0.10 M KNO_3 with 0.10 M KOH solution. The measured pH was then converted to hydrogen ion concentration, $[H^+]$, according to the equation $-\log [H^+] = pH + \log f_{H^+}$. A value of 13.791 was used for pK_w at 25 °C and ionic strength 0.10 M. All equilibrium calculations were performed by using the computer programs described earlier.[12] This program was provided by Professor A. E. Martell and was a simpler version of the later published BEST program.[13] Slight modifications of the program were achieved by incorporating the possibility of hydrolysis of the lanthanide cations (eq 1). Published values of the equilibrium

$$Ln^{3+} + H_2O \rightleftharpoons LnOH^{2+} + H^+ \qquad (1)$$

quotients for eq 1 were used and were in the log K range of -8.3 to -9.0.[14] Data points with pH greater than 7.6 were not included in the calculation to avoid the possibility of formation of hydroxide-bridged multinuclear species. The average log K values are presented together with the standard deviation calculated from those valid data points.

D. Kinetic Studies. A Durrum-Dionex stopped-flow spectrophotometer interfaced with an OLIS data collection system was used for kinetic measurements. All solutions were made in deionized water. Complexes were made in situ by mixing an appropriate amount of lanthanide salt solution and ligand (slight excess) and adjusting the pH to about 7 with $(CH_3)_4NOH$. The complex concentration in the reaction mixture was kept at ca. 5×10^{-5} M. The buffer solutions were made by using a constant acetate ion concentration and varying [acetic acid]. The reaction mixture generally contained 5×10^{-3} M acetate. The ionic strength was adjusted to 0.10 M with $LiClO_4$.

As the lanthanide complexes do not show appreciable absorption in the near-UV or visible region, copper(II) was used as the scavenger of free ligand and the reaction kinetics were followed by monitoring the growth in absorbance due to copper complex at 270 nm. Although the observed dissociation rates for the complexes are independent of $[Cu^{2+}]$, a pseudo-first-order (20-fold) excess of Cu^{2+} (1×10^{-3} M) was used in reaction mixtures.

The solutions in the drive syringes of the stopped-flow spectrophotometer, one containing complex solution and the other containing buffer, $LiClO_4$ and Cu^{2+}, were preequilibrated at the required temperature, which was maintained to ±0.2 °C with a Lauda-Brinkmann (Model K-2/RD) refrigerated water bath and a heat exchanger. Reactions were generally followed up to 3–5 half-lives. Plots of log $(A_\infty - A_t)$ vs time were linear for at least 3 half-lives of reaction. Rate constants quoted represent the average values of at least three kinetic runs and were reproducible within 5%.

Results and Discussion

A. Potentiometric Studies. Equilibrium titration curves (not shown) of ligands alone and of mixtures with 1 equiv of a metal salt were all typical. The calculated pK_a values for the two nitrogen protons for each ligand are shown in Table I, consistent with those of the structural analogues.[1,2] In particular, the values for K22DP are almost identical with those reported earlier.[10]

Table I. Logarithmic Protonation Constants and Stability Constants of K22DA, K22MA, K22DP, and K22MP and Their Metal Complexes[a]

	log K			
	K22DA[b]	K22MA	K22DP	K22MP
H^+				
log K_1	8.45	8.80	8.97	9.01
log K_2	7.80	7.26	8.16	7.79
Ni^{2+}	7.39	5.38	nm	nm
Cu^{2+}	14.49	10.52	8.18	6~7
Zn^{2+}	8.42	5.44	nm	nm
Cd^{2+}	11.07	7.82	6.11	nm
Pb^{2+}	13.55	10.42	9.20	8.09
La^{3+}	12.21	6.62	6.18	nm
Ce^{3+}	12.23	6.84	6.85	nm
Pr^{3+}	12.22	7.04	7.16	nm
Nd^{3+}	12.21	7.24	7.40	nm
Sm^{3+}	12.12	7.51	7.44	nm
Eu^{3+}	12.02	7.38	7.38	nm
Gd^{3+}	11.93	7.29	7.02	nm
Tb^{3+}	11.70	7.23	7.10	nm
Dy^{3+}	11.57	7.15	6.70	nm
Ho^{3+}	11.18	6.91	6.47	nm
Er^{3+}	11.30	6.70	6.20	nm
Tm^{3+}	11.10	6.49	6.13	nm
Yb^{3+}	10.90	6.39	6.10	nm
Lu^{3+}	10.84	6.01	~6	nm

[a] K for H^+: $K_1 = [HL]/[H][L]$, $K_2 = [H_2L]/[H][HL]$. K for metal complex: $K^M{}_{ML} = [ML]/[M][L]$. The ionic strength was 0.10 M, and the temperature was 25.0 ± 0.1 °C. Standard deviations are all within ±0.10 log K unit. nm = not measurable. [b] Data taken from ref 1.

Table I also summarizes the values of the stability constants of all lanthanide complexes of K22DP and K22MA. The data for some selected divalent transition-metal and Pb(II) complexes and those of K22DA are included as well for comparison. It is noted that all values are somewhat lower than those of K22DA reported earlier, indicating the weak complexation ability of the ligands. In fact, the compound K22MP is too weak a ligand for the pH titration method to be useful for the determination of the stability constants for most metal ions except Pb^{2+}. The metal ions hydrolyze and form hydroxide precipitates before any measurable complexation takes place. This phenomenon is also observed in a few occasions for K22DP and K22MA.

Although the ligands studied all have a common 18-membered macrocyclic ring with four ether oxygen and two amine nitrogen donor atoms, the thermodynamic contribution for complexation stability by the macrocycles may not be the same in each case. This is because the pendant ionizable functional group(s) on the macrocycle may add additional stability by chelate ring formation, Coulombic interaction, alteration of ligand conformation upon complexation, etc. and some effects may be synergistic. Careful examination of the data leads to the following conclusions:

1. For a particular lanthanide or transition-metal ion, complex stability varies as K22DA > K22MA ≈ K22DP > K22MP. The greater complexation ability of K22DA as compared to that of K22MA can be easily related to the presence of an additional ionizable acetic acid group, which will form an additional chelate ring with the central metal ion. The additional Coulombic interaction and the occupation of eight coordination sites for K22DA are certainly more advantageous.

2. The weak complexation of K22DP as compared to that of K22DA for all metal ions studied must be related to the reduced thermodynamic stability of the six-membered propionate chelate ring formation of K22DP complexes as compared to that of the five-membered acetate chelate ring formation of K22DA complexes.

3. It is normally expected that the two carboxylic acid groups on K22DP should impose greater Coulombic interaction with the central metal ion as compared to that of K22MA. However, the

---

[12] Chang, C. A.; Douglas, B. E. *J. Coord. Chem.* **1981**, *11*, 91–97.

[13] Motekaitis, R. J.; Martell, A. E. *Can. J. Chem.* **1982**, *60*, 2403–2409.

[14] Baes, C. F.; Mesmer, R. E. *The Hydrolysis of Cations*; Wiley-Interscience: New York, 1976; p 137.

Table II. [Cu^{2+}] Independence of Ln–K22DP and Ln–K22MA Dissociation Kinetics[a] (k_{obsd}, s^{-1})

	$10^3[Cu^{2+}]$, M					
	0.4	0.8	1.0	1.6	2.4	3.2
K22DP						
La	0.204 ± 0.011	0.214 ± 0.003	0.223 ± 0.002	0.225 ± 0.021	0.207 ± 0.002	
Eu	0.012 ± 0.001	0.011 ± 0.001	0.012 ± 0.000	0.010 ± 0.000	0.011 ± 0.000	
Lu	0.615 ± 0.001	0.608 ± 0.003	0.612 ± 0.005	0.617 ± 0.003	0.611 ± 0.002	
K22MA						
La	0.838 ± 0.052	0.800 ± 0.037	0.943 ± 0.021	1.07 ± 0.008	0.929 ± 0.139	0.923 ± 0.139
Eu	0.230 ± 0.023	0.182 ± 0.006	0.237 ± 0.028	0.252 ± 0.020	0.239 ± 0.022	0.243 ± 0.021

[a] Conditions: $[Ln^{3+}] = [L] = 5 \times 10^{-5}$ M, $[H^+] = 1.07 \times 10^{-6}$ M.

Table III. Dependence of Dissociation Kinetics (k_{obsd}, s^{-1}) of Lanthanide Complexes of K22DP and K22MA[a]

	$10^5[H^+]$, M									
	0.085	0.12	0.162	0.19	0.525	0.76	2.51	2.95	6.61	8.13
K22DP										
La		0.223		0.212		0.226		0.253	0.380	...
Eu		0.011		0.011		0.010		0.012	0.013	0.014
Lu		0.619		0.677		...		...	...	...
K22MA										
La	0.945		0.984		1.01		1.06	1.19	1.93	...
Eu	0.216		0.245		0.324		0.376	0.443	0.597	0.631

[a] Conditions: $[Ln^{3+}] = [L] = 5 \times 10^{-5}$ M, $[Cu^{2+}] = 1 \times 10^{-3}$ M.

stability constants of the complexes formed with these two ligands are actually very similar for all lanthanide ions. Two reasons may be involved: First, the five-membered chelate ring formed in the case of K22MA is thermodynamically more favorable. Second, it is very likely that, due to steric factors involved in the complexation of K22DP, the two propionate groups may not coordinate to the central metal ion to a full extent; i.e., there is longer metal–oxygen bond distance. The latter point is further verified by the fact that the stability constants of all transition-metal and lead(II) ions of K22MA are greater than those of K22DP.

4. Another interesting observation is that, with K22DA as the ligand, log $K_{Cu^{2+}}$ (14.49) is greater than log $K_{Pb^{2+}}$ (13.55) whereas, with K22DP as the ligand, log $K_{Cu^{2+}}$ (8.18) is smaller than log $K_{Pb^{2+}}$ (9.20). The possible explanation is that the steric factors for both metals are unfavorable for K22DP as compared to those with K22DA. But, due to the larger ionic radius of Pb^{2+} (1.29 Å) compared to that of Cu^{2+} (0.73 Å), the steric constraints for the formation of a six-membered chelate ring for Pb^{2+} is not as unfavorable as for Cu^{2+}. It is very likely that the Cu^{II}–K22DP complex is a distorted-octahedral one and the Pb^{II}–K22DP complex has more than six coordination sites.

B. Dissociation Kinetics of Complexes. Because of the relatively low formation stabilities of lanthanide complexes of both K22DP and K22MA, an appreciable amount of the ligands remained uncomplexed when $[Ln^{3+}] = [\text{ligand}] = 5 \times 10^{-5}$ M. Thus, two reactions have been observed when the Ln–ligand solution is mixed with the Cu^{2+} scavenger solution at various pH values. A fast reaction corresponds to the complex formation of the uncomplexed ligand with Cu^{2+} ion, viz.

$$Cu^{2+} + H_2L \rightarrow CuL + 2H^+ \qquad (2)$$

The observed rate constants of the fast reaction are at least 25 $M^{-1}\,s^{-1}$ under all the experimental conditions and as expected (1) are independent of the lanthanide metal ion present in the solution, (2) increase as [H^+] decreases, and (3) increase as [Cu^{2+}] increases. Since the present work is concerned mainly with lanthanide complex dissociation kinetics, the Cu^{2+}–K22DP and –K22MA complex formation studies will be reported elsewhere.

The other reaction, a slow one, is indeed the lanthanide complex dissociation, the rate of which is dependent on the lanthanide metal ion present in the solution, viz.

$$LnL^+ + Cu^{2+} \rightarrow CuL + Ln^{3+} \qquad (3)$$

The kinetic events can be easily monitored by the growth of the Cu^{II}–ligand complex band at 270 nm because the time course involved in the dissociation reaction is at least 10 times slower than that of the Cu(II) complex formation reaction except for some Lu^{III}–complex cases.

Table IV. Resolved Rate Constants for Dissociation of Lanthanide Complexes of K22MA and K22DP

	k_d	k_H
K22DP		
La	0.206 ± 0.011	(2.45 ± 0.33) × 10^3
Eu	0.011 ± 0.000	(4.30 ± 0.52) × 10
Lu	0.612 ± 0.003[a]	
K22MA		
La	0.88 ± 0.07	(1.42 ± 0.23) × 10^4
Eu	0.25 ± 0.02	(4.93 ± 0.46) × 10^3
Lu	3.99 ± 1.30[a]	

[a] Data obtained at pH 6.05 and $[Cu^{2+}] = 4 \times 10^{-4}$ M.

1. Effect of [Cu^{2+}] on k_{obsd}. The rates of dissociation are zero order with respect to Cu(II) concentration (Table II). This suggests that the rate-determining step does not involve the formation of any Ln^{III}–ligand–Cu^{II} binuclear species. This is consistent with our earlier suggestion that, for complexes of rigid and sterically crowded ligand such as macrocyclic compounds, the contribution from metal-catalyzed pathways in metal-exchange reactions could be minimal.[5]

2. Acid-Independent and Acid-Dependent Pathways. Table III lists the observed rate constants for the lanthanide complex dissociation reactions at various [H^+] values. In all cases, the plots of k_{obsd} vs [H^+] give straight lines, which suggest the rate law

$$k_{obsd} = k_d + k_H[H^+] \qquad (4)$$

The values of the acid-independent rate constant (k_d) and the acid-dependent rate constant (k_H) are resolved by weighted least-squares analysis and are listed in Table IV.

The trend observed for k_d and k_H values as a function of lanthanide complex formation stability is similar to those found for other lanthanide complexes of both macrocyclic and noncyclic ligands, i.e. the stronger the complex formation, the smaller the rate constant. The absolute values of k_d and k_H for both K22DP and K22MA complexes are greater than those of the corresponding complexes of K22DA and K21DA. The trend for the observed rates is

$$\text{K22MA} > \text{K22DP} > \text{K21DA} > \text{K22DA}$$

This is also expected according to the relative complex formation stabilities.

3. Mechanistic Implications. It was proposed previously that, for lanthanide complexes with relatively rigid ligand backbones such as Ln(CyDTA)$^-$ (CyDTA = *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetate ion), Ln(K22DA)$^+$, and Ln(K21DA)$^+$, the acid-independent pathway involved a slow, rate-determining distortion of the complex, followed by rapid attack of a second metal ion (e.g. Cu^{2+}) or a proton.[4,5,15] The lanthanide ion in the distorted complex still binds to a portion of the ligand, presumably due to the rigid ligand structure and the relatively high formation stability. In the present case, because none of the ligands, i.e. K22MA and K22DP, form very strong complexes with lanthanide ions, the formation of the intermediate distorted complex may no longer be rate-determining. The extremes of the mechanisms may be those of alkali-metal neutral crown ether complexes, i.e. unimolecular dissociative and bimolecular cation interchange (associative),[16,17] which are beyond the scope of the present study.

Acknowledgment. This material was prepared with the support of the U.S. Department of Energy (Grant No. DE-FG05-84ER13292); however, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the view of DOE.

Registry No. K22MA, 82353-42-2; K22DP, 68670-15-5; K22MP, 115290-72-7.

---

(15) Nyssen, G. A.; Margerum, D. W. *Inorg. Chem.* **1970**, *8*, 1814–1820.

(16) Strasser, B. O.; Hallenga, K.; Popov, A. I. *J. Am. Chem. Soc.* **1985**, *107*, 789–792.

(17) Delville, A.; Stover, H. D. H.; Detellier, C. *J. Am. Chem. Soc.* **1987**, *109*, 7293–7301.

Contribution from the Lehrstuhl für Anorganische Chemie I, Ruhr-Universität, D-4630 Bochum, FRG, and Anorganisch-Chemisches Institut, Universität Heidelberg, D-6900 Heidelberg, FRG

Synthesis and Reactivity of $[LRe(NO)(CO)(NCO)]^+$ (L = 1,4,7-Triazacyclononane). Kinetics and Mechanisms of Its Formation and Transformation to $[LRe(NO)(CO)X]^{n+}$ (X = NH_3, Cl, HCO_2^-, $CF_3SO_3^-$) and Other Species. Crystal Structure of $[LRe(NO)(CO)(NH_3)]Br_2$

Christa Pomp,[1a] Karl Wieghardt,*,[1a] Bernhard Nuber,[1b] and Johannes Weiss[1b]

Received February 29, 1988

The complex $[LRe(NO)(CO)(NCO)](BF_4)$ (**1**) has been synthesized from $[LRe(NO)(CO)_2](BF_4)_2$ (L = 1,4,7-triazacyclononane, $C_6H_{15}N_3$) in methanol with a variety of nucleophiles such as $N_2H_4{\cdot}H_2O$, $H_2NNH(CH_3)$, $H_2NN(CH_3)_2$, H_2NOH, and N_3^-. The kinetics and mechanisms of the formation of **1** have been investigated. A general mechanism for these reactions is proposed: nucleophilic attack at a coordinated carbonyl produces carbazoyl intermediates when hydrazine or its N-methylated derivatives are reactants. In the rate-determining step, NH_3, $NH_2(CH_3)$, or $NH(CH_3)_2$ is then cleaved off and fast rearrangement to the N-coordinated isocyanate occurs. **1** undergoes a series of reactions at the coordinated isocyanate ligand; e.g. concentrated HBr reacts in CH_3OH with **1** to produce $[LRe(NO)(CO)(NH_3)]Br_2$ (**3**), the crystal structure of which has been determined by X-ray crystallography. Crystal data: monoclinic; space group $P2_1/c$; a = 10.138 (4), b = 11.507 (5), and c = 12.839 (4) Å; β = 91.86 (3)°; V = 1497.0 (8) Å^3; Z = 4. The kinetics and mechanisms of the reaction of **1** with H^+ to produce **3** and CO_2 have been investigated. **3** is electrochemically or chemically oxidized to paramagnetic $[LRe(NO)(CO)(NH_3)]Br_3$. Concentrated formic acid and trifluoromethanesulfonic acid react with **1** to produce $[LRe(NO)(CO)(HCO_2)]^+$ and $[LRe(NO)(CO)(CF_3SO_3)]^+$. In the presence of iodide anions **1** undergoes addition reactions in methanol or ethanol to form complexes containing coordinated methyl- or ethylcarbamato ligands, $[LRe(NO)(CO)\{NHCO(OR)\}]I$. The latter complexes react in methanol with $NO[BF_4]$ to yield coordinated *N*-nitrosocarbamato ligands, $[LRe(NO)(CO)\{NH(NO)CO(OCH_3)\}](BF_4)_2$. $[LRe(NO)(CO)_2](BF_4)_2$ reacts with $(CH_3)_3NO$ in stoichiometric amounts (1:1) in acetonitrile to produce $[LRe(NO)(CO)(CH_3CN)]^{2+}$ and CO_2 whereas in acetone (a weaker donor solvent) $[LRe(NO)(CO)(N(CH_3)_3)]^{2+}$ is formed. Spectroscopic properties (^1H and ^{13}C NMR, UV–vis, IR) are reported for all compounds.

Introduction

Recently we have reported the synthesis, crystal structures, and reactivity of a series of rhenium(I) tricarbonyl complexes containing tridentate macrocyclic ligands such as 1,4,7-triazacyclononane, 1,4,7-trimethyl-1,4,7-triazacyclononane and 1,4,7-trithiacyclononane.[2–4] These compounds are readily available in excellent yields. The thermodynamic and kinetic stability of the coordinated macrocycles render them good starting materials for rhenium complexes in low and high oxidation states. Thus the reaction of $[LRe(CO)_3]^+$ with $NO[BF_4]$ yields air- and water-stable $[LRe(NO)(CO)_2]^{2+}$, which reacts with $NaBH_4$ yielding $[LRe(NO)(CO)(CH_3)]^{+3}$, whereas with H_2O_2 the latter compound gives $[LReO_3]^+$ (L = 1,4,7-triazacyclononane throughout this paper).[2]

Here we wish to report the kinetics and mechanism of the reactions between $[LRe(NO)(CO)_2]^{2+}$ and hydrazine, methylhydrazine, and *N*,*N*-dimethylhydrazine, hydroxylamine, and azide, all of which yeild the N-coordinated isocyanato complex $[LRe(NO)(CO)(NCO)]^+$ (**1**) (Scheme I). N-Coordinated isocyanato complexes of rhenium have been characterized previously.[12,13] In organometallic chemistry the reaction between these nucleophiles and $M(CO)_6$ (M = Cr, Mo, W) (and other carbonyl complexes) producing $M(CO)_5(NCO)^-$ complexes is well-known.[5–10] For the reaction with azide, kinetic data have been reported.[8,11]

Nucleophilic attack at the C atom of the carbonyl ligand in **1** by nucleophiles such as N_2H_4, NH_2OH, and N_3^- is believed to produce the intermediates A, B, and C (Scheme I). In some instances coordinated carbazoyl intermediates have been isolated or were characterized by infrared spectroscopy in solution.[7,8,14–16]

---

(1) (a) Ruhr-Universität. (b) Universität Heidelberg.

(2) Wieghardt, K.; Pomp, C.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 1659–1661.

(3) Pomp, C.; Duddeck, H.; Wieghardt, K.; Nuber, B.; Weiss, J. *Angew. Chem.* **1987**, *99*, 927–930; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 924–927.

(4) Pomp, C.; Drüeke, S.; Küppers, H.-J.; Wieghardt, K.; Krüger, C.; Nuber, B.; Weiss, J. *Z. Naturforsch.* **1988**, *43B*, 140–146.

(5) Beck, W.; Smedal, H. S. *Angew. Chem.* **1966**, *78*, 267–268.

(6) Beck, W.; Lindenberg, B. *Angew. Chem.* **1970**, *82*, 701.

(7) Angelici, R. J.; Busetto, L. *J. Am. Chem. Soc.* **1969**, *91*, 3197–3200.

(8) Beck, W.; Werner, H.; Engelmann, H.; Smedal, H. S. *Chem. Ber.* **1968**, *101*, 2143–2152.

(9) Saillant, R. B. *J. Organomet. Chem.* **1972**, *39*, C71.

(10) Moelwyn-Hughes, J. T.; Garner, A. W. B.; Howard, A. S. *J. Chem. Soc. A* **1971**, 2361.

(11) Werner, H.; Beck, W.; Engelmann, H. *Inorg. Chim. Acta* **1969**, *3*, 331–334.

(12) Barrientos-Penna, C. F.; Klahn-Oliva, A. H.; Sutton, D. *Organometallics* **1985**, *4*, 367–373.

(13) Angelici, R. J.; Faber, G. C. *Inorg. Chem.* **1971**, *10*, 514–517.

0020-1669/88/1327-3789$01.50/0