to relieve electronic charge, namely the μ-CO arrangement. This permits charge delocalization by a σ-type of bonding. Thus, the 16-electron compound $[Pd_2(\mu\text{-CO})_2Cl_4]^{2-}$ is more stable with respect to the other two possibilities: the 16-electron species $[Pd_2(CO)_2Cl_4]^{2-}$ (all groups terminal with a metal–metal bond, as experimentally found[16] in the case of platinum) and the 18-electron complex $[Pd_2(CO)_2(\mu\text{-Cl})_2Cl_2]^{2-}$. The latter is clearly unfavorable for electron-rich metals lacking an efficient mechanism of π-back-donation.

If a σ-type of bonding is essentially operative for palladium in its binding to CO, decreasing the oxidation state does not necessarily correspond to the stabilization of Pd–CO$_t$ bonds. Further support to this assumption can be obtained from the experimentally observed low stability[24] of $Pd(CO)_4$ as compared to that of $Ni(CO)_4$ in spite of the lower enthalpy of sublimation of palladium (91 kcal/mol) with respect to that of nickel (103 kcal/mol).[25]

Note should also be taken of the apparently peculiar nature of chemisorbed CO on palladium. On this metal, bridging carbonyl groups have been detected spectroscopically[26] and suggested to contribute considerably to the coverage of the surface. This sets an example of how the information from molecular homogeneous systems can sometimes be transferred with some confidence to heterogeneous systems.

These considerations, together with our earlier findings on gold(I) carbonyl complexes,[27] suggest that for late and heavy transition elements, especially those of d^{10} configuration, the mechanism of stabilization of the M–CO$_t$ bond is substantially one of σ-donation to the metal. This makes the carbonyl carbon especially prone to nucleophilic attack, as evidenced by the high reactivity of these carbonyl complexes toward water and amines.[28]

Once certain requirements are met (availability of empty valence orbitals with subsequent sufficient Lewis acidity of the metal center), σ-bonding of CO should not be too surprising, though still uncommon. A few examples of compounds of this type, for which a simple description in terms of σ-bonding appears to be in order, are the d^0 $ZrCp_2(CO)H_2$ and $HfCp_2(CO)H_2$[29] (ν_{CO} 2044 and 2036 cm^{-1}, respectively) and $BH_3(CO)$[30] (ν_{CO} 2165 cm^{-1}).

Summary

Contrary to $Pd_2(CO)_2(\mu\text{-Cl})_2Cl_2$, which is unreactive toward CO, the corresponding platinum(II) dimer reacts promptly with CO at atmospheric pressure and room temperature to give *cis*-$Pt(CO)_2Cl_2$. It has been shown that the reaction proceeds via the intermediate formation of the kinetically controlled trans isomer, which has been isolated and characterized by analysis, IR spectroscopy, and ^{195}Pt NMR spectroscopy. These results are discussed within the framework of the general problem of metal–terminal CO bonds for elements of the nickel triad. Other things being equal, the Pd–

CO$_t$ bond appears to be inherently weaker than the corresponding bonds for nickel and platinum, due to lack of an efficient π-back-bonding mechanism. Thus, palladium shows little transitional behavior in its combination with CO. This result is expected in view of the position of the metal in the periodic table but has been frequently neglected.

Note Added in Proof. The compound $Pd_{10}(CO)_{14}(PBu_3)_4$ was recently shown[31] to have two terminal carbonyl groups. In our hands, *trans*-$Pt(CO)_2Cl_2$ gave a mixture of *cis*-$Pt(CO)_2Cl_2$ and $Pt_2(CO)_2Cl_4$ by sublimation under reduced pressure (ca. 5×10^{-2} mmHg); cf. ref 32.

Registry No. $Pt(CO)_2(\mu\text{-Cl})_2Cl_2$, 17522-99-5; *trans*-$Pt(CO)_2Cl_2$, 62841-60-5; *cis*-$Pt(CO)_2Cl_2$, 15020-32-3; $(NBu_4)_2PtCl_4$, 21790-80-7; $(Pt(CO)Cl_3^-)$, 21710-57-6; Pt, 7440-06-4; Ni, 7440-02-0; Pd, 7440-05-3.

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Kinetics of the Acid Dissociation of the Copper(II) and Nickel(II) Complexes of 5,7-Dioxo-1,4,8,11-tetraazacyclotetradecane

Robert W. Hay,* Mahesh P. Pujari, and Fiona McLaren

The acid dissociation kinetics of open-chain polyamine complexes have been extensively studied[1–9] and the topic has been reviewed.[10] Currently there is considerable interest in the kinetics and mechanism of the acid dissociation of macrocyclic polyamine complexes.[11–20] For 14-membered tetraaza

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Table I. Acid Dissociation of [CuL] at 25 °C and μ = 0.1 M

pH	$10^5[H^+]$, M	$10^3 k_{obsd}$, s^{-1}	$10^{-7} k_{obsd}/$ $[H^+]^2$, M^{-2} s^{-1}
4.73	2.41	6.68	1.15
4.81	2.01	4.49	1.11
4.87	1.75	3.68	1.21
4.94	1.49	2.59	1.17
5.00	1.30	1.95	1.16
5.05	1.15	1.43	1.07
5.25	0.72	0.60	1.12

ligands these reactions are quite slow,[12,20] and thus the dissociation of the blue copper(II) complex of *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (**1**) occurs at a measurable rate at 25 °C in 1–5 M HNO_3.[19]

1   **2**
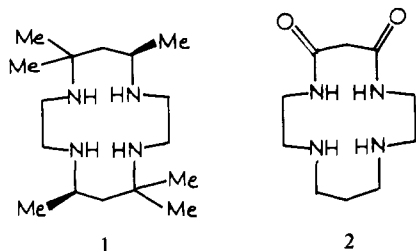
In a previous paper[21] we have described the preparation of the macrocyclic diamide ligand 5,7-dioxo-1,4,8,11,-tetraazacyclotetradecane (**2** = LH_2) and its copper(II) and nickel(II) complexes [ML] (**3**), formed by deprotonation of two amide

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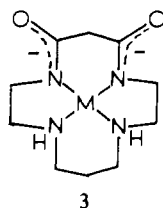
groups. The dissociation of the copper(II) and nickel(II) complexes in acidic solution is quite rapid, and we now discuss the acid dissociation kinetics in detail.

Experimental Section

The ligand 5,7-dioxo-1,4,8,11-tetraazacyclotetradecane (LH_2) and its copper(II) and nickel(II) complexes were prepared as previously described.[21]

The dissociation kinetics were monitored using a pH stat. The equipment and general experimental procedure employed have been outlined.[22] The concentration of the metal complex used in the kinetic study was 5×10^{-4} M, and the titrating acid ($HClO_4$) was 2.5×10^{-2} M. Two moles of acid was consumed per mole of complex in the reaction. The ionic strength was 0.1 M, maintained by using $NaClO_4$. Values of the hydrogen ion concentration were obtained from the pH by using a molar activity coefficient γ_1 of 0.772 at 25 °C estimated by using the Davies equation.[23] Values of k_{obsd}, the observed first-order rate constant, at constant pH were evaluated from the titration data by using a desk-top computer. At the other temperatures employed the appropriate values of γ are 0.774 (20 °C), 0.770 (30 °C), and 0.768 (35 °C).

Results and Discussion

Dissociation of [CuL] was conveniently monitored by pH stat in the pH range 4.73–5.25 at 25 °C and μ = 0.1 M. Two

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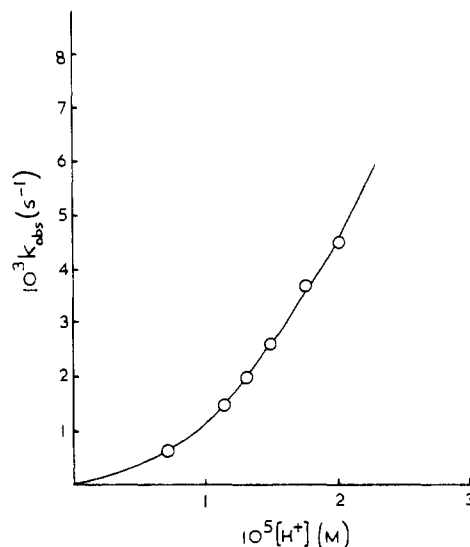(23) Davies, C. W. *J. Chem. Soc.* **1936**, 2093.

**Figure 1.** Dissociation of [CuL] over the pH range 4.73–5.25 at μ = 0.1 M and 25 °C.

Table II. Acid Dissociation of [NiL] at 25 °C and μ = 0.1 M ($NaClO_4$)

pH	$10^5[H^+]$, M	$10^3 k_{obsd}$, s^{-1}	$10^{-5} k_{obsd}/$ $[H^+]^2$, M^{-2} s^{-1}
3.69	26.44	8.52	1.22
3.80	20.53	5.40	1.28
3.90	16.31	3.33	1.25
3.96	14.20	2.43	1.20
4.04	11.81	1.67	1.20
4.09	10.52	1.36	1.23
4.12	9.83	1.18	1.22
4.25	7.28	0.65	1.23
4.40	5.16	0.33	1.24

Table III. Acid Dissociation of [CuL] at 20, 30, and 35 °C and μ = 0.1 M

T, °C	pH	$10^5[H^+]$, M	$10^3 k_{obsd}$, s^{-1}	$10^{-7} k_{obsd}/$ $[H^+]^2$, M^{-2} s^{-1}
20	4.77	2.19	3.31	0.69
	4.87	1.74	2.19	0.72
	4.92	1.55	1.58	0.66
	5.00	1.29	1.14	0.68
	5.05	1.15	0.98	0.74
30	4.95	1.46	4.16	1.95
	4.97	1.39	3.41	1.76
	5.03	1.21	2.79	1.90
	5.08	1.08	2.27	1.95
	5.18	0.86	1.29	1.74
35	4.96	1.43	6.31	3.08
	5.02	1.24	4.62	3.00
	5.13	0.97	3.02	3.21
	5.17	0.88	2.47	3.19

moles of protons was consumed per mole of complex, corresponding to the reaction stoichiometry

$$ML + 2H^+ \rightarrow M^{2+}(aq) + LH_2$$
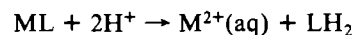
Values of k_{obsd} at various pH values for dissociation of the copper(II) complex are summarized in Table I. Plots of k_{obsd} vs. $[H^+]$ are curved (Figure 1), but plots of k_{obsd} vs. $[H^+]^2$ are linear, confirming a second-order dependence on the hydrogen ion concentration. Least-squares analysis of the data gives $k_{obsd}/[H^+]^2 = (1.15 \pm 0.03) \times 10^7$ M^{-2} s^{-1} at 25 °C and I = 0.1 M. There is no indication of any solvolytic pathway, and dissociation occurs exclusively by an acid dissociation process similar results are obtained with the nickel(II) complex (Table

Table IV. Acid Dissociation of [NiL] at 20, 30, and 35 °C and $\mu = 0.1$ M

T, °C	pH	$10^5[H^+]$, M	$10^3 k_{obsd}$, s^{-1}	$10^5 k_{obsd}/[H^+]^2$, M^{-2} s^{-1}
20	3.74	23.51	4.34	0.79
	3.86	17.84	2.48	0.78
	3.94	14.84	1.72	0.78
	4.12	9.80	0.75	0.78
	4.20	8.15	0.53	0.79
30	3.93	1.53	4.51	1.93
	4.00	1.30	3.33	1.97
	4.07	1.11	2.47	2.00
	4.10	1.03	2.08	1.96
	4.18	0.86	1.49	2.01
35	4.05	1.16	3.97	2.95
	4.10	1.03	3.24	3.05
	4.15	0.92	2.48	2.93
	4.20	0.82	1.99	2.96

II), where $k_{obsd}/[H^+]^2 = (1.23 \pm 0.03) \times 10^5$ M^{-2} s^{-1} at 25 °C and $\mu = 0.1$ M. Dissociation of the copper(II) complex is about 100-fold faster than that of the nickel(II) complex. Slower dissociation of the planar d^8 complex is expected.

The kinetic data establish that two protons are involved in the transition state of the reaction. Dissociation of the copper(II) complex of the 14-membered macrocyclic amide complex differs quite markedly from that of 14-membered tetraaza macrocycles. The latter normally show a first-order dependence on [H$^+$] and often display an acid-independent solvolytic pathway.[19] In addition, the amide complex dissociates much more rapidly in acidic solution. These observations suggest that protonation may first occur on the amide oxygen atoms to give the iminol tautomer (**4**), followed by intramo-

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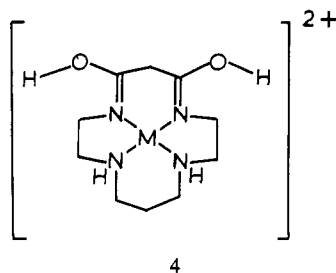
lecular proton transfer to the nitrogen donors. Protonation in strong acid of [Co(NH$_3$)$_4$(glyNH)]$^{2+}$ [24] and [Co(glyglyO)$_2$]$^-$ [25] has been shown to occur at the amide oxygen, rather than the amide nitrogen. X-ray studies[25] of the protonated [Co(glyglyO)$_2$]$^-$ cation indicate that the double-bond character of the carbon–nitrogen bond is increased while that of the carbon–oxygen bond is decreased in accord with the equilibrium
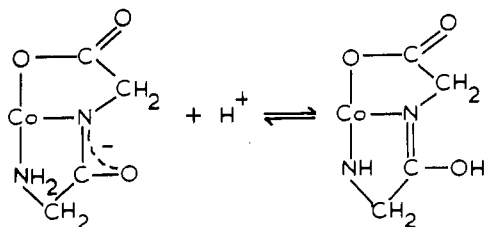
The temperature dependence of the acid-catalyzed dissociation of the copper(II) and nickel(II) complexes was studied at the additional temperatures of 20, 30, and 35 °C, and the data

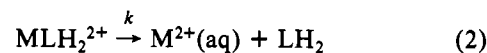(24) Buckingham, D. A.; Foster, D. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 3451.

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Table V. Activation Parameters and Rate Constants for the Acid-Catalyzed Dissociation of [CuL] and [NiL]

compd	T, °C	k_H, M^{-2} s^{-1}
[CuL]^a	20	$(0.68 \pm 0.03) \times 10^7$
	25	$(1.15 \pm 0.03) \times 10^7$
	30	$(1.92 \pm 0.16) \times 10^7$
	35	$(2.97 \pm 0.13) \times 10^7$

$\Delta H^{\ddagger} = 71.7 \pm 1.5$ kJ mol^{-1}; $\Delta S^{\ddagger}_{298} = 131 \pm 5$ J K^{-1} mol^{-1}

[NiL]^b	20	$(0.78 \pm 0.01) \times 10^5$
	25	$(1.23 \pm 0.01) \times 10^5$
	30	$(1.91 \pm 0.03) \times 10^5$
	35	$(2.98 \pm 0.13) \times 10^5$

$\Delta H^{\ddagger} = 64.5 \pm 0.5$ kJ mol^{-1}; $\Delta S^{\ddagger}_{298} = 69 \pm 2$ J K^{-1} mol^{-1}

obtained are summarized in Tables III and IV. Rate constants and activation parameters are collected in Table V. For the dissociation of the copper complex $\Delta H^{\ddagger} = 71.7 \pm 1.5$ kJ mol^{-1} and $\Delta S_{298}^{\ddagger} = 131 \pm 5$ J K^{-1} mol^{-1}, while for the nickel complex $\Delta H^{\ddagger} = 64.5 \pm 0.5$ kJ mol^{-1} and $\Delta S_{298}^{\ddagger} = 69 \pm 2$ J K^{-1} mol^{-1}.

A possible kinetic scheme for the acid dissociation could involve the steps

$$\text{ML} + 2\text{H}^+ \overset{K}{\rightleftharpoons} \text{MLH}_2^{2+} \qquad (1)$$

$$\text{MLH}_2^{2+} \overset{k}{\rightarrow} \text{M}^{2+}(\text{aq}) + \text{LH}_2 \qquad (2)$$

involving a rapid preequilibrium protonation step (eq 1) and a slow rate-determining dissociation (eq 2). It can be readily shown that

$$\text{rate} = \frac{kK[\text{ML}][\text{H}^+]^2}{1 + K[\text{H}^+]^2}$$

$$k_{obsd} = \frac{kK[\text{H}^+]^2}{1 + K[\text{H}^+]^2}$$

Under the conditions of the present experiments $K[\text{H}^+]^2 \ll 1$ and $k_{obsd} = kK[\text{H}^+]^2$ with $k_H = kK = k_{obsd}/[\text{H}^+]^2$. The activation parameters thus relate to combined rate and equilibrium constants. One interesting feature of the acid-catalyzed dissociation of macrocyclic complexes is that multiprotonation of the complex is often required for the dissociation of the ligand to occur. Thus, we have previously shown[14] that dissociation of the pentaaza macrocycle [15]-ane-N$_5$ (**5**) from copper(II) and nickel(II) involves a second-

5 **6**
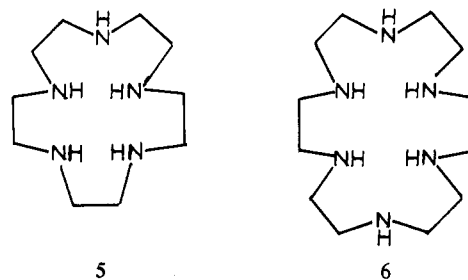
order dependence on [H$^+$], while dissociation of [18]-ane-N$_6$ (**6**) involves a third-order dependence on [H$^+$]. Breaking of the second or third metal–nitrogen bond may well be the rate-determining step in some of these reactions.

Registry No. 3 (M = Cu), 72547-88-7; 3 (M = Ni), 74994-10-8.