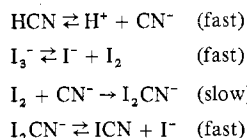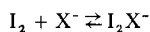$$\text{rate} = k_1 \frac{[\text{HCN}][\text{I}_3^-]}{[\text{H}^+][\text{I}^-]}$$

was not unexpected. The related mechanism is
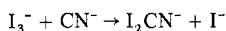
$$\text{HCN} \rightleftarrows \text{H}^+ + \text{CN}^- \quad \text{(fast)}$$

$$\text{I}_3^- \rightleftarrows \text{I}^- + \text{I}_2 \quad \text{(fast)}$$

$$\text{I}_2 + \text{CN}^- \rightarrow \text{I}_2\text{CN}^- \quad \text{(slow)}$$

$$\text{I}_2\text{CN}^- \rightleftarrows \text{ICN} + \text{I}^- \quad \text{(fast)}$$

with the intermediate I_2CN^- being postulated in analogy to I_2Cl^-, etc.

The second term is surprising, since the intermediate I_2X^- generally arises from the mechanistic step

$$\text{I}_2 + \text{X}^- \rightleftarrows \text{I}_2\text{X}^-$$

as in the third step above. In the k_2 term, however, the formation of I_2CN^- must come about by direct displacement

$$\text{I}_3^- + \text{CN}^- \rightarrow \text{I}_2\text{CN}^- + \text{I}^-$$

Using the values $k_1 = 2.55 \times 10^{-3}$ M s^{-1}, $K_{\text{I}_3^-} = 870$ M^{-1}, and $K_{\text{HCN}} = 4.8 \times 10^{-10}$ M, it is possible to estimate the rate constant for the step

$$\text{I}_2 + \text{CN}^- \rightarrow \text{I}_2\text{CN}^-$$
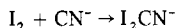
The value so obtained is 3×10^9 M^{-1} s^{-1}. Similarly, the constant for the step

$$\text{I}_3^- + \text{CN}^- \rightarrow \text{I}_2\text{CN}^- + \text{I}^-$$
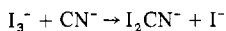
can be estimated from k_2 (0.740 s^{-1}) and K_{HCN}; this gives the value 4×10^8 M^{-1} s^{-1}. Neither step indicates reaction at every collision, but they are very rapid steps indeed.

Experimental Section

All chemicals used were of reagent grade and the laboratory-distilled water was further purified by passage through a mixed-bed ion-exchange column. Potassium iodide was kept at least 50 times in excess of iodine, solutions being prepared immediately prior to the kinetic studies. Hydrogen ion concentrations were measured on a Leeds and Northrup pH meter.

The kinetics of the reaction were followed at a single wavelength, 350 nm, using a Durrum D-110 stopped-flow spectrophotometer, all temperatures being maintained to within ±0.2 °C. The output of the photomultiplier of the stopped-flow served as input to the A/D converter of a PDP-8/e computer and as input to a storage-type oscillosope. The computer, through locally designed software and hardware, was used to convert the voltage output of the photomultiplier to absorbance vs. time data. One hundred data points were collected in each kinetic run. The rate at which the photomultiplier was sampled was a function of the rate of the reaction of interest. The rate of sampling was chosen such that the reaction was followed to 90% completion. The absorbance vs. time data were then processed on line, using a linear least-squares technique, to yield pseudo-first-order rate constants. All reported rate constants are averages of at least ten kinetic runs.

Appendix A

The iodide ion dependence indicates a two term-rate law of the form

$$k_{\text{obsd}} = \frac{k_1'}{[\text{I}^-]} + k_2'$$

where the primes indicate pseudo constants. This form can be obtained from the rate law

$$-\frac{d[\text{I}_3^-]}{dt} = k_1 \frac{[\text{HCN}][\text{I}_3^-]}{[\text{H}^+][\text{I}^-]} + k_2 \frac{[\text{HCN}][\text{I}_3^-]}{[\text{H}^+]}$$

With all other concentrations much larger than $[\text{I}_3^-]$ the latter equation can be rewritten as

$$-\frac{d \ln [\text{I}_3^-]}{dt} = \left\{ \frac{k_1}{[\text{I}^-]} + k_2 \right\} \frac{[\text{HCN}]}{[\text{H}^+]}$$

so that

$$k_{\text{obsd}} = \left\{ \frac{k_1}{[\text{I}^-]} + k_2 \right\} \frac{[\text{HCN}]}{[\text{H}^+]}$$

which has the requisite form.

Registry No. I_3^-, 14900-04-0; HCN, 74-90-8; I^-, 20461-54-5.

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Contribution from the Department of Chemistry and Biochemistry, James Cook University of North Queensland, Townsville, Queensland 4811, Australia

Studies Involving Nitrogen–Oxygen Donor Macrocyclic Ligands. 2. Copper(II), Zinc(II), and Cadmium(II) Complexes of Cyclic Tetradentate Ligands Derived from Salicylaldehyde[1]

L. F. Lindoy,* H. C. Lip, L. F. Power, and J. H. Rea

A large number of metal complex studies involving polyether macrocycles of the "crown" type have now been reported.[2] Such ligands incorporate a number of oxygen donors (typically five or more) in a large-ring system and often exhibit novel coordination behavior particularly toward certain non transition metal ions such as the alkali and alkaline earths.[2]

A second category of macrocyclic ligands[3] consists of those ligands which contain nitrogen, sulfur, or (more recently[4]) phosphorus donor atoms. Of these, tetradentate ligands containing four nitrogen donor atoms have been studied in most detail and such ligands often resemble the natural macrocycles (for example, the porphyrins or corrins) in their coordination behavior.[5]

Only a few cyclic ligands of intermediate structure between the "crown" ethers and the second category of macrocycles mentioned above have been reported and the coordination behavior of these intermediate ligands toward a range of metal ions has received much less attention up to the present.[2,3] In view of the often special properties associated with each of the above main ligand categories, it is of considerable intrinsic interest to investigate both the transition and non transition metal chemistry of ligands which fall between these main categories. The work now reported forms part of an overall study in this general area.

The macrocycles used for the present study are of structure I. The syntheses, properties, and some reactions of the nickel
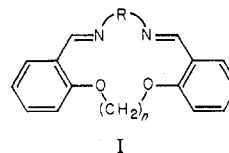
I

|	Abbreviations	
R	when $n = 2$	when $n = 3$
$-(\text{CH}_2)_2-$	O-en-N-en	O-tn-N-en
$-(\text{CH}_2)_3-$	O-en-N-tn	O-tn-N-tn
$-\text{CH}_2\text{CH}(\text{CH}_3)-$	O-en-N-pn	

complexes of ligands of type I have been discussed in part 1

Table I. Analytical Data for the Complexes

	% C		% H		% N		% metal	
Complex	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
[Cu(O-en-N-tn)](ClO₄)₂	39.97	39.98	3.56	3.63	4.89	4.73	11.13	11.3
[Cu(O-en-N-tn)Cl]ClO₄	45.02	44.91	3.97	4.01	5.52	5.47	12.53	12.8
[Cu(O-en-N-tn)NCS]ClO₄	45.37	45.21	3.82	4.13	7.92	7.95	12.00	12.0
[Cu(O-en-N-tn)Br]ClO₄	41.37	41.13	3.66	3.57	5.08	4.87	11.53	11.3
[Cu(O-en-N-tn)Br]BF₄	42.37	42.53	3.75	3.89	5.21	5.51	11.79	11.6
[Cu(O-en-N-tn)Br]PF₆	38.22	37.79	3.37	3.45	4.69	4.74	10.64	10.7
[Cu(O-tn-N-tn)](ClO₄)₂	41.07	41.34	3.80	4.08	4.77	4.50		
[Cu(O-tn-N-tn)Cl]ClO₄	46.09	45.78	4.28	4.49	5.38	5.20	12.20	12.2
[Cu(O-tn-N-tn)NCS]ClO₄	46.39	45.78	4.08	4.11	7.73	7.63	11.69	11.6
[Zn(O-en-N-en)Cl₂]	50.21	50.34	4.21	4.39	6.51	6.32	15.25	15.2
[Zn(O-en-N-pn)Cl₂]ᵃ	51.33	51.75	4.55	4.92	6.28	5.85	14.66	14.7
[Zn(O-tn-N-en)Cl₂]	51.33	51.19	4.55	5.10	6.28	6.18	14.70	15.0
[Cd(O-en-N-tn)₂](ClO₄)₂·H₂O	48.26	48.22	4.49	4.61	5.93	6.02		
[Cd(O-en-N-pn)₂](ClO₄)₂·¹/₂H₂O	48.70	49.03	4.41	4.33	5.99	5.98		

ᵃ Percent Cl: calcd, 15.94; found, 15.9.

of this series.[1] An extension of this investigation to include copper(II), zinc(II), and cadmium(II) is now reported. Although open-chain Schiff base derivatives prepared by condensation of salicylaldehyde with an amine constitute one of the most studied groups of ligands,[6] only one other macrocyclic ligand of this type, namely, II, has been reported previously.[7]

II
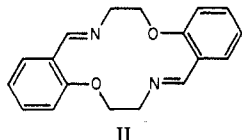
Experimental Section

Analyses for carbon, hydrogen, nitrogen, and chloride were determined by Mr. J. Kent of the Microanalytical Laboratory, University of Queensland, or by the Australian Microanalytical Service, Melbourne. Copper was determined volumetrically by the iodine–thiosulfate method. Zinc was determined by EDTA titration. Infrared spectra were recorded on a Jasco IRA-I spectrophotometer using Nujol mulls. Reflectance spectra in the visible–near-infrared range were determined by Dr. G. M. Mockler of the University of Wollongong using a Zeiss PMQII spectrophotometer fitted with an RA3 reflectance attachment. Magnetic moments were determined by the Gouy method using HgCo(NCS)₄ as calibrant. Conductance measurements were obtained using a Philips bridge, Model PR9501. The syntheses of the two dialdehyde precursors, as well as the free macrocycles O-en-N-tn and O-tn-N-tn, have been described previously.[1] All complexes were dried over P₄O₁₀ in vacuo before analyses.

Preparation of Complexes of Type [Cu(macrocycle)](ClO₄)₂ Where macrocycle = O-en-N-tn or O-tn-N-tn. Ligand (0.3 g) in hot methanol (30 ml) was added to a stirred boiling solution of copper(II) perchlorate hexahydrate (1.1 g) in hot methanol (30 ml). The solution was filtered and then let stand whereupon the product crystallized. The product was washed with methanol and then ether.

Preparation of Complexes of Type [Cu(O-en-N-tn)X]ClO₄ Where X = Cl, Br, or NCS. Ligand (0.3 g) in hot methanol (30 ml) was added to a stirred boiling solution of a mixture of copper(II) perchlorate hexahydrate (0.4 g) and the lithium halide (0.1 g) or potassium thiocyanate (0.1 g) in methanol (50 ml). The hot solution was filtered and then allowed to cool. The product which crystallized was washed with methanol and then ether.

Preparation of Complexes of Type [Cu(O-tn-N-tn)X]ClO₄ Where X = Cl or NCS. A procedure similar to that above was employed, except that ethanol was substituted for methanol as the reaction solvent.

Preparation of Complexes of the Type [Cu(O-en-N-tn)Br]Y Where Y = BF₄ or PF₆. A procedure similar to that used to prepare complexes of the type [Cu(O-en-N-tn)X]ClO₄ was employed, except that copper(II) nitrate trihydrate (0.2 g) was substituted for copper(II) perchlorate hexahydrate and sodium tetrafluoroborate (0.2 g) or potassium hexafluorophosphate (0.2 g) in hot methanol (40 ml) was added to the hot reaction solution to cause precipitation of the product.

Preparation of Complexes of the Type Zn(macrocycle)Cl₂ Where macrocycle = O-en-N-en, O-en-N-pn, or O-tn-N-en. 1,2-Diaminoethane (0.24 g) or 1,2-diaminopropane (0.26 g) in hot methanol (40

ml) was added to a stirred boiling solution of 1,4-bis(2-formylphenyl)-1,4-dioxabutane[1] (1.08 g) or 1,5-bis(2'-formylphenyl)-1,5-dioxapentane[1] (1.14 g) and zinc(II) chloride (0.58 g) in methanol (150 ml) whereupon, in each case, a white microcrystalline product separated. This was filtered off and washed with methanol and then ether.

Preparation of [Cd(O-en-N-tn)₂](ClO₄)₂·H₂O. O-en-N-tn (0.75 g) in methanol (50 ml) was added, drop by drop over 3 h, to a hot stirred solution of cadmium acetate dihydrate (0.7 g) and lithium perchlorate (0.7 g) in methanol. As the solution cooled, a small amount of white precipitate formed which was filtered off and discarded. The filtrate was concentrated and an off-white product crystallized on standing. It was washed with hot methanol and then ether.

Preparation of [Cd(O-en-N-pn)₂](ClO₄)₂·¹/₂H₂O. 1,2-Diaminopropane (0.20 g) in methanol (30 ml) was added dropwise, over 4 h, to a hot stirred solution of 1,4-bis(2'-formylphenyl)-1,4-dioxabutane (0.70 g), cadmium acetate dihydrate (0.70 g), and lithium perchlorate (0.7 g) in methanol (150 ml). The off-white microcrystalline product was isolated and washed with hot methanol and then ether.

Analytical data for the complexes are listed in Table I.

Results and Discussion

A series of copper(II), zinc(II), and cadmium(II) complexes of 14–16-membered macrocycles of type I have been synthesized using both direct and in situ procedures. Table II lists a range of data for the compounds. With respect to ligand absorptions, the infrared spectra of all of the complexes are quite similar to those obtained previously for the corresponding nickel complexes[1] and do not contain absorptions attributable to amine or aldehyde groups. Such spectra thus indicate that the complexes contain the respective cyclic ligands intact.

Copper Complexes. Copper complexes of two ligands, O-en-N-tn and O-tn-N-tn, have been prepared. All of the complexes show copper to ligand ratios of 1:1. The ν₃ and ν₄ perchlorate modes of the complexes of type [Cu(macrocycle)X]ClO₄ each occur as a single strong absorption which is typical of noncoordinated perchlorate anions.[8] These spectra contrast with the spectra of diperchlorate complexes in which the ν₃ modes are each split into two absorptions. Splitting of this type can result from a lowering of the symmetry by crystal packing or hydrogen-bonding effects;[9] however it may alternatively reflect that the symmetry of one or both perchlorate groups in each complex is lowered by coordination to the copper ion. Many examples of such behavior are known for copper complexes and a number of x-ray structure determinations of copper(II) complexes containing bound perchlorate ions have been reported.[10] The positions of the ν(C=N) modes in the spectra of [Cu(O-en-N-tn)NCS]ClO₄ (2120 cm⁻¹) and [Cu(O-tn-N-tn)NCS]ClO₄ (2090 cm⁻¹) are both consistent with the thiocyanates being N bonded and terminal[11]. Owing to ligand absorptions in the same region, assignment of the ν(C—S) modes for these compounds could not be made with certainty.

Table II. Properties of the Macrocyclic-Ligand Complexes

Complex	Color	Molar conduct-ance,[a,b] ohm^{-1} cm^2 mol^{-1}	Magnetic moment,[c] μ_B	Selected ir data, cm^{-1} ν(C=N)	ClO$_4^-$ modes ν_3	ν_4
[Cu(O-en-N-tn)](ClO$_4$)$_2$	Green	310	1.88 (24)	1635	1105, 1055	620
[Cu(O-en-N-tn)Cl]ClO$_4$	Green	145	1.86 (25)	1640	1085	620
[Cu(O-en-N-tn)NCS]ClO$_4$	Olive green	155	1.79 (28)	1630	1085	620
[Cu(O-en-N-tn)Br]ClO$_4$	Green	156	1.84 (28)	1640	1085	620
[Cu(O-en-N-tn)Br]BF$_4$	Green	157	1.85 (28)	1635	1050^d	
[Cu(O-en-N-tn)Br]PF$_6$	Green	146	1.80 (24)	1640		
[Cu(O-tn-N-tn)](ClO$_4$)$_2$	Green	311	1.91 (23)	1635	1055, 1110	620
[Cu(O-tn-N-tn)Cl]ClO$_4$	Green	148	1.89 (24)	1640	1085	620
[Cu(O-tn-N-tn)NCS]ClO$_4$	Olive green	152	1.91 (23)	1635	1085	620
[Zn(O-en-N-en)Cl$_2$]	Off-white	Insol		1625		
[Zn(O-en-N-pn)Cl$_2$]	Off-white	Insol		1625		
[Zn(O-tn-N-en)Cl$_2$]	Off-white	Insol		1630		
[Cd(O-en-N-tn)$_2$](ClO$_4$)$_2$·H$_2$O	Off-white	274		1635	1080	620
[Cd(O-en-N-pn)$_2$](ClO$_4$)$_2$·$^1/_2$H$_2$O	Off-white	296		1635	1090	620

^{a} Concentration ~1 × 10^{-3} M in acetonitrile at 24 °C. ^{b} Range for 1:1 electrolyte ca. 120–160 ohm^{-1} cm^2 mol^{-1}; range for 2:1 electrolyte ca. 220–300 ohm^{-1} cm^2 mol^{-1}. ^{c} Temperature (°C) in parentheses. ^{d} BF$_4$ mode.
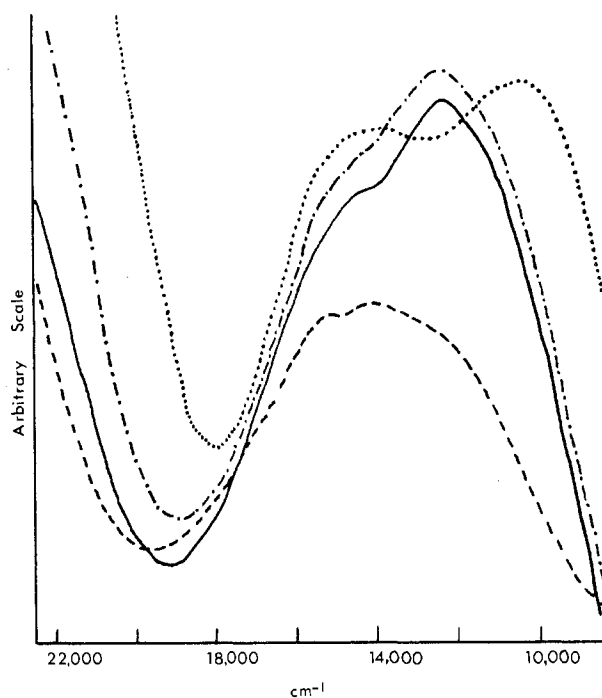

Figure 1. Visible–near-infrared reflectance spectra for copper complexes of O-en-N-tn: - - - -, [Cu(O-en-N-tn)](ClO$_4$)$_2$; · · · · ·, [Cu(O-en-N-tn)NCS]ClO$_4$; ———, [Cu(O-en-N-tn)](ClO$_4$)$_2$; - · - · -, [Cu(O-en-N-tn)Br]ClO$_4$.

Figure 2. Visible–near-infrared reflectance spectra for copper complexes of O-tn-N-tn: - - - -, [Cu(O-tn-N-tn)](ClO$_4$)$_2$; ———, [Cu(O-tn-N-tn)Cl]ClO$_4$; - · - · -, [Cu(O-tn-N-tn)NCS]ClO$_4$.

All complexes have room-temperature magnetic moments (Table II) in the range expected for copper(II) with $S = ^1/_2$.

Conductance measurements (Table II) show that both of the diperchlorate complexes are 2:1 electrolytes in acetonitrile whereas the remaining complexes are 1:1 electrolytes.[12,13] If weak coordination of perchlorate ions in the diperchlorate complexes does occur in the solid (as suggested by the infrared spectra), then the conductance data remain consistent with this fact since acetonitrile is known to displace weakly coordinated ligands from the coordination sphere in other complexes.[13] The above conductance results strongly suggest that the haloperchlorate complexes are five-coordinate in solution. Further evidence for five-coordination is provided by the results of a conductometric titration of [Cu(O-en-N-tn)](ClO$_4$)$_2$ (1.0 × 10^{-3} M in acetonitrile) with tetraethylammonium bromide (5.0 × 10^{-3} M in acetonitrile). A distinct 1:1 end point indicating the formation of a formally five-
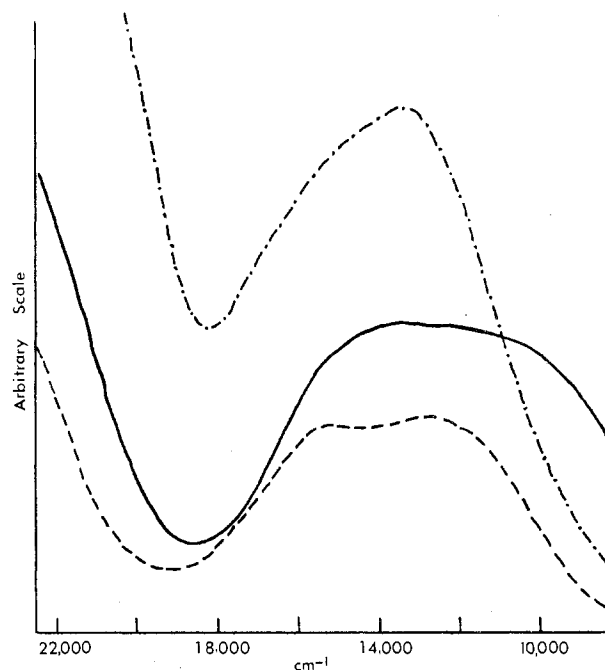
coordinate cation was obtained. No tendency toward coordination of a second bromide ion was detected. Five-coordination in the complex cation also appears to persist in the solid state since salts of the type [Cu(O-en-N-tn)Br]X (where X$^-$ is any one of ClO$_4^-$, BF$_4^-$, or PF$_6^-$, viz., a large anion of low coordinating ability) can be isolated readily. These three salts all give identical visible reflectance spectra. Similarly, a range of perchlorate salts of other related five-coordinate cations have been isolated (Table II). As mentioned previously, the infrared spectra of these salts confirm the presence of ionic perchlorate groups.

Because of the inherent rigidity of each half of the respective macrocyclic ligands, coordination around the copper ion in an essentially planar configuration should occur readily. It thus seems most likely that the above five-coordinate complexes will approach a square-pyramidal geometry in which the coordinating anion occupies the axial site. Nevertheless many related compounds exhibit distortions toward a trigonal-bipyramidal geometry such that an "intermediate" structure

results[10,14] and it is not possible to predict the degree of such distortions in the present case.

The reflectance spectra of a selection of the complexes of O-en-N-tn and O-tn-N-tn are reproduced in Figures 1 and 2, respectively. All spectra show a broad envelope of bands in the 18 000–8000-cm^{-1} region. Although for strictly C_{4v} symmetry three d–d transitions are expected ($^2B_1 \rightarrow {}^2A_1$, $^2B_1 \rightarrow {}^2B_2$, $^2B_1 \rightarrow {}^2E_1$),[15] it is not possible to make reliable spectral assignments for the compounds discussed here owing to the broadness of the observed spectra and the respective complexes. As has been pointed out elsewhere,[16] caution should be exercised when attempting to assign stereochemistries to copper(II) complexes solely on the basis of visible spectra.

Zinc and Cadmium Complexes. Three zinc complexes (Table II) containing 14- or 15-membered macrocyclic rings have been prepared by in situ reaction in methanol of the appropriate diamine and dialdehyde in the presence of zinc chloride. Attempts to prepare zinc chloride complexes of a number of other ligands of type I yielded products which tended to be hygroscopic and which were not obtained analytically pure. These latter products proved difficult to purify and were not studied further.

Owing to the insolubility of the zinc complexes in suitable solvents, no conductance data could be obtained. Nevertheless it seems most likely that these complexes are octahedral—a geometry which is quite common for other related zinc complexes.[17]

Two cadmium perchlorate complexes were obtained analytically pure.[18] Both of these were found to have cadmium to ligand ratios of 1:2 even though they were prepared in the presence of excess metal ion. The tendency of cadmium to combine with two ligands may be a reflection of its greater ionic radius when compared with the other ions used so far.[19] It is difficult, in the absence of structural data, to decide whether or not the cadmium ion is too large to be encircled by these cyclic ligands. Uncertainty exists as to whether covalent or ionic radii are more appropriate for estimation of the effective metal ion radius in small-ring compounds of the present type which contain donors of such widely differing character as unsaturated nitrogen and ether oxygen atoms. The conductance data (Table II) together with the infrared spectra in the perchlorate region indicate that both compounds contain ionic perchlorate groups. The question of the stereochemistry of these compounds must remain open at present—although the possibility that all donor atoms of both ligands are attached to a single cadmium ion cannot be ruled out. Examples of both seven- and eigh-coordinate cadmium compounds have been reported recently.[20]

Registry No. [Cu(O-en-N-tn)](ClO$_4$)$_2$, 58919-20-3; [Cu(O-en-N-tn)Cl]ClO$_4$, 58919-22-5; [Cu(O-en-N-tn)NCS]ClO$_4$, 58919-24-7; [Cu(O-en-N-tn)Br]ClO$_4$, 58958-10-4; [Cu(O-en-N-tn)Br]BF$_4$, 58919-26-9; [Cu(O-en-N-tn)Br]PF$_6$, 58919-27-0; [Cu(O-tn-N-tn)](ClO$_4$)$_2$, 58919-29-2; [Cu(O-tn-N-tn)Cl]ClO$_4$, 58919-31-6; [Cu(O-tn-N-tn)NCS]ClO$_4$, 58919-33-8; [Zn(O-en-N-en)Cl$_2$], 58919-34-9; [Zn(O-en-N-pn)Cl$_2$], 58919-35-0; [Zn(O-tn-N-en)Cl$_2$], 58919-36-1; [Cd(O-en-N-tn)$_2$]ClO$_4$, 58958-11-5; [Cd(O-en-N-pn)$_2$]ClO$_4$, 58958-12-6.

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Contribution from the Department of Chemistry, Kinki University, Higashi-Osaka, Japan.

Stability Enhancement of Mixed-Ligand Copper(II), Nickel(II), and Cobalt(II) Complexes with 2,2'-Bipyridyl and β-Diketonates
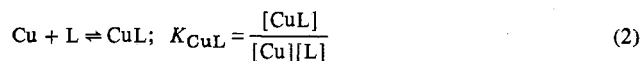
Megumu Munakata,* Mitsuo Harada, and Syozo Niina

Sigel and co-workers[1–8] have reported that the O,O ligands coordinating as dianions form stabler complexes with the Cu–2,2'-bpy 1:1 complex (eq 1) than the hydrated Cu^{2+} ion

$$Cu(bpy) + L \rightleftharpoons Cu(bpy)L; \quad K_{Cu(bpy)L} = \frac{[Cu(bpy)L]}{[Cu(bpy)][L]} \quad (1)$$
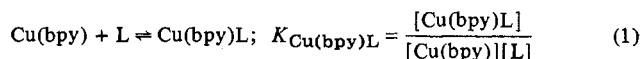
(eq 2). Consequently, positive Δ log K values were observed

$$Cu + L \rightleftharpoons CuL; \quad K_{CuL} = \frac{[CuL]}{[Cu][L]} \quad (2)$$

(eq 3) (bpy and L represent 2,2'-bipyridyl and ligand, re-

$$\Delta \log K = \log K_{Cu(bpy)L} - \log K_{CuL} = \log K_{Cu(L)bpy} - \log K_{Cu(bpy)} \quad (3)$$

spectively.) This is worth noting, since the first-step formation constant K_{ML} is usually larger than the second-step formation constant K_{ML_2}: $K_{ML} > K_{ML_2}$. The ternary complex having such high stability is also of interest in connection with the formation of the ternary enzyme–metal ion–substrate complex in an enzymatic reaction.

We wish now to report on the formation constant for the reactions between the M^{2+}–bpy 1:1 complex (M^{2+} = Cu^{2+}, Ni^{2+}, Co^{2+}) and monoanions of β-diketones and on the driving forces which lead to the formation of mixed-ligand complexes.

Experimental Section

Reagents. Acetylacetone, benzoylacetone, dibenzoylmethane, dipivaloylmethane, and 2,2'-bipyridyl were obtained from the Dojindo Co. Ltd.; 2-(2-pyridyl)imidazole[9] and 2-(2-pyridyl)benzimidazole[10]