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]

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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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(19) Effective ionic radii (Å): Cd^{2+}, 0.95; Cu^{2+}, 0.73; Zn^{2+}, 0.75. For convenience, six-coordinate values are compared. Values are taken from R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **26**, 1046 (1970).
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Stability Enhancement of Mixed-Ligand Copper(II), Nickel(II), and Cobalt(II) Complexes with 2,2′-Bipyridyl and β-Diketonates

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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

$$\mathrm{Cu(bpy)} + \mathrm{L} \rightleftharpoons \mathrm{Cu(bpy)L}; \quad K_{\mathrm{Cu(bpy)L}} = \frac{[\mathrm{Cu(bpy)L}]}{[\mathrm{Cu(bpy)}][\mathrm{L}]} \tag{1}$$

(eq 2). Consequently, positive Δ log *K* values were observed

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

(eq 3) (bpy and L represent 2,2′-bipyridyl and ligand, respectively.)

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

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]

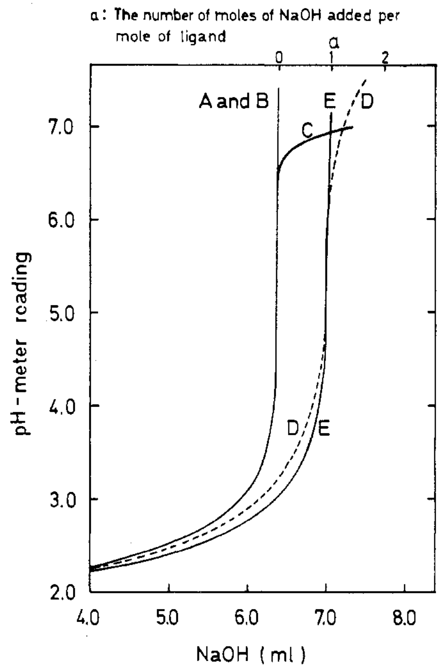

Figure 1. Titration curve (60% dioxane): (A) acid, (B) acid-acetylacetone, (C) acid-Cu^{2+}-2,2′-bipyridyl, (D) acid-Cu^{2+}-acetylacetone, (E) acid-Cu^{2+}-2,2′-bipyridyl-acetylacetone. Conditions: Temperature, 25 °C; NaOH, 0.161 N; acid, 0.0181 N $HClO_4$; Cu^{2+}, 2,2′-bipyridyl, and acetylacetone, 10^{-2} M.

Table I. Logarithms of Stability Constants of the Binary Cu^{2+}-β-diketonate Complexes and the Ternary bpy-Cu^{2+}-β-diketonate Complexes (25 °C, $I = 0.1$ (0.1 M $NaClO_4$), 60% Dioxane)[a]

	β-diketonate			
	acac	bzac	dbm	dpm
$\log K^{Cu}_{Cu(bpy)L}$	10.12	10.65	11.43	13.22
$\log K^{Cu}_{CuL}$	9.61	9.90	10.56	12.05
$\Delta \log K$	+0.51	+0.75	+0.87	+1.17
pK_a	9.89	9.98	10.49	12.82

[a] K_a is the practical dissociation constant of β-diketone; $K_{Cu(bpy)L}$ = [Cu(bpy)L]/[Cu(bpy)][L]; K_{CuL} = [CuL]/[Cu][L]; $\Delta \log K = \log K_{Cu(bpy)L} - \log K_{CuL} = \log K_{Cu(L)bpy} - \log K_{Cu(bpy)}$. L = β-diketonate: acac, acetylacetonate; bzac, benzoylacetonate; dbm, dibenzoylmethanate; dpm, dipivaloylmethanate.

were synthesized as in the literature, respectively. $Cu(ClO_4)_2$ and $HClO_4$ were obtained from Tokyo Kasei Co. Ltd.

Measurements. The titrations were carried out under N_2 in solution with ionic strength $I = 0.1$ ($NaClO_4$) at 25 °C with a Hitachi-Horiba pH meter. The exact Cu^{2+}, Ni^{2+}, and Co^{2+} concentrations of the stock solutions were determined using ethylenediaminetetraacetic acid. All constants in water-dioxane solvents were calculated in accordance with the Irving-Rossotti titration technique.[11]

Results and Discussion

Figure 1 shows the plots of pH meter readings against volume of alkali in the 2,2′-bipyridyl-Cu^{2+}-acetylacetonate system. Cu-bpy 1:1 formation is complete before the pH meter reading 2.5 (in 60% dioxane) and it forms hydroxo complexes at higher pH meter readings up to 6.0. In the pH meter reading region between 2.5 and 6.0, therefore, stability constants of the ternary bpy-Cu^{2+}-ligand complexes were determined by the assumption that in a 1:1 mixture of Cu^{2+} and bpy the formation of the Cu^{2+}-bpy 1:1 complex is complete, as already reported by Sigel et al.[3] The stability constants of other N,N ligand-M^{2+}-β-diketonate systems were also calculated in a pH region where the M^{2+}-N,N ligand 1:1 complex was completely formed and hydroxide was omitted.

Table II. Logarithms of Stability Constants of Binary Cu^{2+}-bzac Complexes and the Ternary N,N Ligand-Cu^{2+}-bzac Complexes (25 °C, $I = 0.1$ (0.1 M $NaClO_4$), 60% Dioxane)[a]

	N,N ligand			
	bpy	pbi	pi	en
$\log K_{Cu(A)bzac}$	10.65	10.34	10.15	8.78
$\log K_{Cu\ bzac}$	9.90	9.90	9.90	9.90
$\Delta \log K$	+0.75	0.44	+0.25	−1.20

[a] A = N,N ligand: bpy, 2,2′-bipyridyl; pbi, 2-(2-pyridyl)benzimidazole; pi, 2-(2-pyridyl)imidazole, en, ethylenediamine.

Table III. Logarithms of Stability Constants of the Binary M^{2+}-β-diketonate Complexes and the Ternary bpy-M^{2+}-β-diketonate Complexes (25 °C, $I = 0.1$ (0.1 M $NaClO_4$), 60% Dioxane)[a]

	β-diketonate		
	acac	bzac	dbm
$\log K_{Ni(bpy)\ L}$	6.71	7.20	7.98
$\log K_{NiL}$	6.89	7.13	7.73
$\Delta \log K$	−0.18	+0.07	+0.25
$\log K_{Co(bpy)\ L}$	0.22	6.60	7.22
$\log K_{CoL}$	0.26	6.57	7.18
$\Delta \log K$	−0.04	+0.03	+0.04

[a] L = β-diketonate.

The dissociation constants of β-diketones, the stability constants of the binary Cu^{2+}-β-diketonate complexes and the ternary bpy-Cu^{2+}-β-diketonate complexes, and Δ log K values calculated according to eq 3 are given in Table I. Positive Δ log K values are observed in these systems and increase in the order acetylacetonate (acac) < benzoylacetonate (bzac) < dibenzoylmethanate (dbm) < dipivaloylmethanate (dpm), which is also the increasing order of those pK_a values, namely, the basicities. This shows that β-diketonates coordinating as monoanions also form stabler complexes with the Cu^{2+}-bpy 1:1 complex than with the hydrated Cu^{2+} ion. Further, the Δ log K values for bpy-Cu^{2+}-dbm (+0.87) and bpy-Cu^{2+}-dpm (+1.17) systems are larger than the values for bpy-Cu^{2+}-pyrocatecholate (+0.43)[7] and bpy-Cu^{2+}-dihydroxynaphthalene-2-sulfonate (+0.69)[7] systems. The stability of ternary N,N ligand-Cu^{2+}-benzoylacetonate complexes increases by changing the N,N ligand to ethylenediamine < 2-(2-pyridyl)imidazole < 2-(2-pyridyl)benzimidazole < 2,2′-bipyridyl, as shown in Table II. The given series is an order of increasing π-acceptor qualities (dπ-pπ back-donation), as have been reported by Sigel et al.[4]

The stability constants of the binary Co^{2+} (and Ni^{2+}) complexes with β-diketonates and the ternary bpy-Co^{2+} (and Ni^{2+})-β-diketonate complexes and Δ log K values are summarized in Table III. The Δ log K values are negative for the bpy-Co^{2+}-acac and bpy-Ni^{2+}-acac systems, whereas positive values are obtained for bpy-Co^{2+}-bzac, bpy-Ni^{2+}-bzac, bpy-Co^{2+}-dbm, and bpy-Ni^{2+}-dbm systems. In these systems, the Δ log K values also increase with increasing the basicity of β-diketones [acac < bzac < dbm], though the dependency of Δ log K on ligand basicity in ternary complexes is complicated.[12] The stability constants for bpy-Co^{2+} (and Ni^{2+})-dbm systems were not obtained, since the hydroxo complexes of Ni(II) and Co(II) were formed. It is noted that the Δ log K values for the bpy-M^{2+}-bzac and the bpy-M^{2+}-dbm systems increase in the order $Co^{2+} < Ni^{2+} < Cu^{2+}$.

It is concluded from these results that the stability constants for the N,N ligand-metal(II) ion-β-diketonate systems are enhanced as the basicity of the β-diketonates and the π-acceptor qualities of the *N,N* ligand increase.

Registry No. $Cu(acac)^+(aq)$, 58919-10-1; $Cu(bzac)^+(aq)$, 58919-11-2; $Cu(dbm)^+(aq)$, 58919-12-3; $Cu(dpm)^+(aq)$, 58918-80-2; $Cu(bpy)(acac)^+(aq)$, 58918-81-3; $Cu(bpy)(bzac)^+(aq)$, 58918-82-4;

Cu(bpy)(dbm)$^+$(aq), 58918-83-5; Cu(bpy)(dpm)$^+$(aq), 58918-84-6; Cu(pbi)(bzac)$^+$(aq), 58918-85-7; Cu(pi)(bzac)$^+$(aq), 58918-86-8; Cu(en)(bzac)$^+$(aq), 58918-87-9; Ni(acac)$^+$(aq), 58918-88-0; Ni(bzac)$^+$(aq), 58918-89-1; Ni(dbm)$^+$(aq), 58918-90-4; Ni(bpy)(acac)$^+$(aq), 58918-91-5; Ni(bpy)(bzac)$^+$(aq), 58918-92-6; Ni(bpy)(dbm)$^+$(aq), 58918-93-7; Co(acac)$^+$(aq), 58918-94-8; Co(bzac)$^+$(aq), 58918-95-9; Co(dbm)$^+$(aq), 58918-96-0; Co(bpy)(acac)$^+$(aq), 58918-97-1; Co(bpy)(bzac)$^+$(aq), 58918-98-2; Co(bpy)(dbm)$^+$(aq), 58918-99-3.

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Crystallization of Amorphous GeTe under Pressure

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Two phases of GeTe were crystallized from amorphous thick films of 1:1 composition prepared by cathode vapor deposition.[2a] The crystallization was initiated in an opposed-anvils, high-pressure apparatus.[2b] Special care was taken to conform with the recommended sample thickness-to-diameter ratio so as to ensure uniform pressure distribution.[3] A graphical summary is presented in Figure 1.

It will be noted that at temperatures below 300 °C no crystallization resulted at pressures up to 120 kbars and for times up to 51 h at conditions as shown in Table I. However, from about 300 °C and above, the known rhombic phase (GeTe-I) and a new, orthorhombic phase of GeTe (GeTe-II) were quenched from the indicated experimental conditions.

The x-ray *d* spacings (Cu Kα) of GeTe-I agree well with the data of Schubert and Fricke,[4] who described the phase as having a trigonally distorted sodium chloride structure. The *d* spacings for GeTe-II may be indexed on the basis of an orthorhombic unit cell, type *Pnma*, with $a = 10.95$, $b = 4.03$, and $c = 4.45$ Å (Table II).

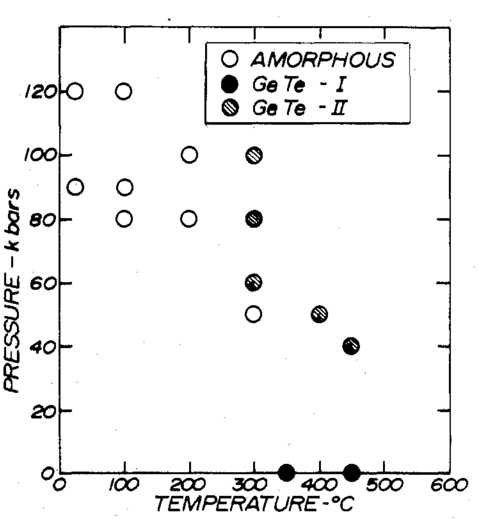

Figure 1. Results after quenching samples of amorphous 1:1 Ge:Te composition held at the *P–T* conditions as plotted.

Table I. Experimental Conditions

Pressure, kbars	Temp, °C	Time, h	Result
			Amorphous Thick Film
100	300	19	100% GeTe-II
90	25	19	Noncrystallized
100	200	20	Noncrystallized
90	100	20	Noncrystallized
80	300	26	100% GeTe-II
80	100	26	Noncrystallized
120	100	51	Noncrystallized
120	25	51	Noncrystallized
60	300	31	90% GeTe-II, 10% GeTe-I
50	300	31	Noncrystallized
50	400	15	95% GeTe-II, 5% GeTe-I
40	450	15	80% GeTe-II, 20% GeTe-I
0	350	24	100% GeTe-I
0	450	24	100% GeTe-I
			Powder of Amorphous Film
120	100	15	Noncrystallized
120	25	15	Noncrystallized
80	200	15	Noncrystallized

Table II. X-Ray *d* Spacings for GeTe-II[a]

hkl	d_{obsd}	d_{calcd}	*I*
201 (011)	3.15	3.18	60
111	2.90	2.89	100
400	2.730	2.740	20
211	2.589	2.601	20
311	2.433	2.423	20
112 (302)	1.924	1.924	20
220	1.870	1.885	60
600	1.824	1.830	20
511	1.767	1.770	80
312	1.720	1.721	20
701	1.481	1.480	40
113	1.383	1.384	40

[a] $a = 10.95$ Å, $b = 4.03$ Å, $c = 4.45$ Å, and $V = 1.96.4$ Å^3 (orthorhombic *Pnma*).

Discussion

One reason for starting with an amorphous material in studies of this type is that an intermediate or metastable phase might be encountered that would be of theoretical interest with respect to kinetics, free energy of formation, topotaxy, and other features. However, in the case of GeTe-II we believe that the phase may be stable in the *P–T* region in which it was found. This conclusion is not based on the rigorous criteria of reversibility because the experiments were not of sufficient number and design to permit a close determination of phase boundaries. Rather, it is based on the general concurrence of behavior of the series GeS, GeSe, and GeTe-II with the series SnS, SnSe, and SnTe, all of which are of the orthorhombic structure type *Pnma*. The systematic relationships of the cell parameters of the two series are shown in Figures 2 and 3. The volume of the rhombic GeTe-I (*Z* also 4) is shown in Figure 3 for comparison as being the less dense, low-pressure phase and not consistent with the series of orthorhombic phases.

In a study[5] of the system SnTe–GeTe, lattice parameters, obtained by x-ray diffraction of samples under high pressure, are given for compositions from 0 to 35 mol % GeTe. The phases were all isostructural with our GeTe-II. By extrap-