

Contribution from the Department of Chemistry,  
Tulane University, New Orleans, Louisiana 70118

### Infrared and Structural Studies of $M^I M^{II} X_3$ Type Transition Metal Halides

G. L. McPherson\* and Jin Rong Chang

Received July 11, 1972

A large number of double salts of the  $M^I M^{II} X_3$  type (where  $M^I$  is a large univalent cation,  $M^{II}$  a divalent metal ion, and X a halide ion) have been prepared and characterized. When X is chloride or bromide, these salts commonly adopt the hexagonal,  $CsNiCl_3$  structure which consists of linear parallel chains of octahedra sharing faces with the  $M^{II}$  ions at the centers, the halide ions at the corners, and the  $M^I$  ions at positions between chains. The spectroscopic and magnetic properties of these hexagonal salts are currently of interest because the compounds are thought to be linear antiferromagnets.<sup>1-3</sup>

A systematic investigation of the infrared spectra of the  $M^I M^{II} X_3$  (where X is Cl, Br, or I) was undertaken to determine how sensitive the spectra are to structural variations and to look for trends in the metal-halogen stretching frequencies. A number of previously unreported  $M^I M^{II} X_3$  compounds were prepared and used in this study. The crystallographic properties as well as the infrared spectra of several of the salts were investigated.

#### Experimental Section

**Preparation of Compounds.** The salts  $CsNiCl_3$ ,  $RbNiCl_3$ ,  $CsNiBr_3$ ,  $CsNiI_3$ , and  $CsCuCl_3$  were crystallized by slow evaporation from hot concentrated aqueous solutions of the appropriate hydrogen halide containing the alkali halide and transition metal halide in a 1:1 mole ratio.

The salts  $CsMnCl_3$  and  $CsMnBr_3$  were prepared by dehydration of the hydrated double salts in a stream of the hydrogen halide at 600°. The hydrated double salts were crystallized from aqueous solutions of the appropriate halides.

The remaining salts  $CsCoCl_3$ ,  $CsFeCl_3$ ,  $CsCrCl_3$ ,  $CsVCl_3$ ,  $CsMgCl_3$ ,  $TiNiCl_3$ , and  $KNiCl_3$  were prepared by fusing equimolar mixtures of the monovalent halide and the anhydrous dihalide in evacuated quartz ampoules. The anhydrous  $FeCl_2$ ,  $CoCl_2$ , and  $NiCl_2$  were prepared from the hydrated salts by heating to 600° in a stream of dry HCl. The anhydrous  $VCl_2$  and  $MgCl_2$  were purchased commercially. Most of these compounds are quite water sensitive and must be handled in a dry atmosphere. Analyses are presented in Table I.

**Infrared Spectra.** The samples were studied as Nujol mulls between polyethylene plates. The spectra were recorded from 33 to 400  $cm^{-1}$  on a Beckman IR-11.

**Crystallographic Studies.** Crystals of  $CsNiI_3$  were grown from hot concentrated HI solutions. Crystals of  $TiNiCl_3$  and  $KNiCl_3$  were grown from melts by the Bridgeman method. The details of the procedure have been reported previously.<sup>4</sup> Small crystals suitable for X-ray study were cleaved from larger crystals and sealed in 0.3-mm glass capillaries. Precession photographs of the  $h0l$ ,  $h1l$ ,  $hhl$ , and  $h(h+1)l$  zones were taken with molybdenum  $K\alpha$  radiation. All four salts crystallize in hexagonal lattices with systematic absences of  $hhl$ ,  $l \neq 2n$ .

The densities of the salts determined by pycnometric methods agree quite well with densities calculated from the number of molecules per unit cell ( $Z$ ) and the lattice constants ( $\rho_o = 5.10, 5.21$ , and  $2.76$  g/ml and  $\rho_c = 5.06, 5.14$ , and  $2.86$  g/ml for  $CsNiI_3$ ,  $TiNiCl_3$ , and  $KNiCl_3$ , respectively). Crystallographic data are given in Table II.

Table I. Analytical Data

Compd	% halogen		Compd	% halogen	
	Calcd	Found		Calcd	Found
$CsMgCl_3$	40.4	39.9	$CsCuCl_3$	35.2	35.0
$CsVCl_3$	36.2	36.1	$RbNiCl_3$	42.5	42.5
$CsCrCl_3$	36.5	35.9	$KNiCl_3$	53.3	53.0
$CsMnCl_3$	36.1	35.9	$TiNiCl_3$	28.8	29.0
$CsFeCl_3$	36.0	35.8	$CsMnBr_3$	56.1	55.7
$CsCoCl_3$	35.7	35.5	$CsNiBr_3$	55.6	55.7
$CsNiCl_3$	35.7	35.8	$CsNiI_3$	66.5	66.1

Table II. Crystallographic Data

Compd	Space group	Lattice constants, Å			Ref
		<i>a</i>	<i>c</i>	<i>Z</i>	
$CsMgCl_3$	$P6_3/mmc$	7.269	6.187	2	<i>a</i>
$CsVCl_3$	$P6_3/mmc$	7.23	6.03	2	<i>b</i>
$CsCrCl_3$	$(P6_3mc)$	7.256	6.224	2	<i>c</i>
$CsMnCl_3$	$R3m$	7.290	27.317	9	<i>d</i>
$CsFeCl_3$	$P6_3/mmc$	7.24	6.05	2	<i>e</i>
$CsCoCl_3$	$P6_3/mmc$	7.20	6.03	2	<i>f</i>
$CsNiCl_3$	$P6_3/mmc$	7.18	5.93	2	<i>g</i>
$CsCuCl_3$	$P6_3$	7.2157	18.1777	6	<i>h</i>
$RbNiCl_3$	$P6_3/mmc$	6.96	5.91	2	<i>i</i>
$KNiCl_3$	$P6_3/mmc$	13.57	5.95	8	This work
$TiNiCl_3$	$P6_3/mmc$	6.85	5.88	2	This work
$CsMnBr_3$	$P6_3/mmc$	7.609	6.52	2	<i>j</i>
$CsNiBr_3$	$P6_3/mmc$	7.50	6.24	2	<i>k</i>
$CsNiI_3$	$P6_3/mmc$	8.00	6.77	2	This work

<sup>a</sup> Reference 4. <sup>b</sup> H. J. Seifert and P. Ehrlich, *Z. Anorg. Allg. Chem.*, **302**, 284 (1959). <sup>c</sup> G. L. McPherson, T. J. Kistenmacher, J. B. Folkers, G. D. Stucky, *J. Chem. Phys.*, in press. <sup>d</sup> T. Li, G. D. Stucky, G. L. McPherson, *Acta Crystallogr.*, in press. <sup>e</sup> H. J. Seifert and K. Klatyk, *Z. Anorg. Allg. Chem.*, **341**, 1 (1966). <sup>f</sup> H. Soling, *Acta Chem. Scand.*, **22**, 2793 (1966). <sup>g</sup> G. N. Tischenko, *Tr. Inst. Kristallogr., Akad. Nauk SSSR*, **11**, 93 (1955). <sup>h</sup> A. W. Schlueter, R. A. Jacobson, and R. E. Rundle, *Inorg. Chem.*, **5**, 277 (1966). <sup>i</sup> R. W. Asmussen, T. K. Larson, and H. Soling, *Acta Chem. Scand.*, **23**, 2055 (1969). <sup>j</sup> J. Goodyear and D. J. Kennedy, *Acta Crystallogr., Sect. B*, **28**, 1640 (1972). <sup>k</sup> G. D. Stucky, S. D'Agostino, and G. McPherson, *J. Amer. Chem. Soc.*, **88**, 4828 (1966).

#### Results and Discussion

**Crystallography.** Of the  $M^I M^{II} X_3$  salts used in this study (see Table II) the most commonly occurring structure is the  $CsNiCl_3$  structure ( $P6_3/mmc$ ;  $Z = 2$ ). The salts  $CsCuCl_3$ ,  $CsMnCl_3$ ,  $CsCrCl_3$ , and  $KNiCl_3$  are the exceptions. The structure of the copper salt has been shown to consist of chains of octahedra sharing faces in which the copper ions are not located at the centers but form a helical array about the sixfold screw axis which passes through the center of the chain.<sup>5</sup> The  $CsMnCl_3$  structure can be described as a combination of octahedra sharing faces and corners.<sup>6-9</sup> Three  $MnCl_6$  octahedra share faces forming a linear  $Mn_3Cl_{12}^{6-}$  unit which then shares corners with six other  $Mn_3Cl_{12}^{6-}$  groups. Crystallographic studies indicate that the structure of  $CsCrCl_3$  is similar to that of  $CsNiCl_3$ , but the geometry of the anionic chain appears to be somewhat different. The X-ray data do not distinguish with certainty between a model in which the chloride ions are disordered about the mirror plane perpendicular to the *c* axis and an ordered model in which the positions of the chloride ions are shifted along the *c* axis so that the chromium-chlorine-chromium bridging is asymmetric. The

(5) A. W. Schlueter, R. A. Jacobson, and R. E. Rundle, *Inorg. Chem.*, **5**, 277 (1966).

(6) T. Li, G. D. Stucky, and G. L. McPherson, *Acta Crystallogr.*, in press.

(7) M. Kestigian, W. J. Croft, and F. D. Leipziger, *J. Chem. Eng. Data*, **12**, 91 (1967).

(8) H. Rinneberg and H. Hartmann, *J. Chem. Phys.*, **52**, 5814 (1970).

(9) M. Melamud, J. Makovsky, and H. Shaked, *Phys. Rev. B*, **3**, 3873 (1971).

(1) N. Achiwa, *J. Phys. Soc. Jap.*, **27**, 561 (1969).

(2) J. Smith, B. C. Gerstein, S. H. Liu, and G. Stucky, *J. Chem. Phys.*, **53**, 418 (1970).

(3) R. J. Birgeneau, R. Dingle, M. T. Hutchings, G. Shirane, and S. L. Holt, *Phys. Rev. Lett.*, **26**, 718 (1971).

(4) G. L. McPherson, T. J. Kistenmacher, and G. D. Stucky, *J. Chem. Phys.*, **52**, 815 (1970).

Table III. Infrared Frequencies ( $\text{cm}^{-1}$ ) and Assignments<sup>a</sup>

Assignments	Salts of the $\text{CsNiCl}_3$ Type									
	$\text{CsMgCl}_3$	$\text{CsVCl}_3$	$\text{CsFeCl}_3$	$\text{CsCoCl}_3$	$\text{CsNiCl}_3$	$\text{RbNiCl}_3$	$\text{TlNiCl}_3$	$\text{CsNiBr}_3$	$\text{CsMnBr}_3$	$\text{CsNiI}_3$
$E_{1u}(a)$	317 b, s	312 b, s	245 b, s	246 b, s	258 b, s	263 b, m	260 b, s	190 b, s	190 b, s	158 b, m
$A_{2u}(a)$	250 b, s	256 b, s	186 b, s	195 b, s	204 b, s	202 b, m	210 b, s	160 b, s	144 b, s	134 b, m
$E_{1u}(b)$	174 sp, m	162 sp, m	158 sp, m	165 sp, m	179 sp, m	171 m	172 sp, m	115 w	99 w	88 w
$E_{1u}(c)$	82 s	83 m	76 m	78 s	81 s	80 m	60 s	64 s	60 s	55 sp, m
$A_{2u}(b)$	49 sp, m	52 sp, s	52 sp, m	52 sp, m	55 sp, m	51 sp, m	40 sp, m	49 m	42 m	43 sp, w

Other $M^I M^{II} X_3$ Salts							
$\text{CsCrCl}_3$	$\text{CsMnCl}_3$		$\text{CsCuCl}_3^b$			$\text{KNiCl}_3$	
307 b, vs	235 b, s	93 m	288 b, s	158 sp, w	72 m	265 b, s	63 s
260 b, s	200 b, s	72 s	260 b, s	145 b, m	50 m	205 b, s	
163 b, s	158 s	57 sp, m	188 sp, w	111 sh, w		178 m	
76 s	140 w		180 sh, w	95 m		145 w	
47 s	124 s		172 sp, w	80 m		105 b, s	

<sup>a</sup> Key: b, broad; sp, sharp; sh, shoulder; s, strong; m, medium; w, weak. <sup>b</sup> Frequencies of 293, 287, and 263  $\text{cm}^{-1}$  have been reported for the 200–400- $\text{cm}^{-1}$  region of  $\text{CsCuCl}_3$ : D. M. Adams and P. J. Lock, *J. Chem. Soc. A*, 620 (1967).

former seems more reasonable in terms of possible static or dynamic Jahn-Teller effects, but the latter seems to be favored by the structural refinement.<sup>10</sup>

**Infrared Spectra.** Recently Adams and Smardzewski studied the infrared and Raman spectra of  $(\text{CH}_3)_4\text{NMnCl}_3$  and unambiguously assigned the band symmetries from polarized spectra.<sup>11</sup> They observed five infrared-active bands. The three higher energy bands were assigned to internal vibrations of the  $\text{MnCl}_3^-$  anionic chain, while the two lower energy bands were attributed to translatory modes associated with motion of the cations relative to the anionic chains. Although  $\text{CsNiCl}_3$  and  $(\text{CH}_3)_4\text{NMnCl}_3$  do not crystallize in the same space group, the geometries of the  $\text{MCl}_3^-$  chains are very similar in both structures.<sup>12</sup> Factor group analyses by Adams and Smardzewski predict that  $\text{CsNiCl}_3$ , like  $(\text{CH}_3)_4\text{NMnCl}_3$ , will have five ir-active vibrations.

The spectra of the chloride salts having the  $\text{CsNiCl}_3$  structure show a five-band pattern similar to that observed for  $(\text{CH}_3)_4\text{NMnCl}_3$ . The band frequencies and assignments are reported in Table III. The five-band spectrum appears to be quite characteristic of compounds having anionic chains with the same structure as those of  $\text{CsNiCl}_3$  and  $(\text{CH}_3)_4\text{NMnCl}_3$ . Salts which have distinctly dissimilar structures, such as  $\text{CsCuCl}_3$  and  $\text{CsMnCl}_3$ , have considerably different spectra (see Figure 1).

The spectrum of  $\text{CsCrCl}_3$  is of interest in light of the unusual structural properties of the compound. The spectrum contains five bands which appear at frequencies similar to those observed for the chloride salts having the  $\text{CsNiCl}_3$  structure, but the band shapes are somewhat different. The most obvious difference is in the  $E_{1u}(b)$  band which appears in the 150–180- $\text{cm}^{-1}$  region. This band is quite broad and intense in the spectrum of the chromium salt but is less intense and much sharper in the spectra of the  $\text{CsNiCl}_3$  type salts (see Figure 1). Thus, the infrared data support the X-ray findings in that the structure of  $\text{CsCrCl}_3$  appears to be similar to but not identical with the  $\text{CsNiCl}_3$  structure.

The  $M^I M^{II} X_3$  salts are an ideal group of compounds for making spectral comparisons, since most of them have a common structure. Within a series of isostructural compounds, it is possible to observe the variations of the infrared frequencies with changes in cation, metal, and halogen. A

(10) G. L. McPherson, T. J. Kistenmacher, J. B. Folkers, and G. D. Stucky, *J. Chem. Phys.*, in press.

(11) D. M. Adams and R. R. Smardzewski, *Inorg. Chem.*, **10**, 1127 (1971).

(12) B. Morosin and E. J. Graeber, *Acta Crystallogr.*, **23**, 766 (1967).

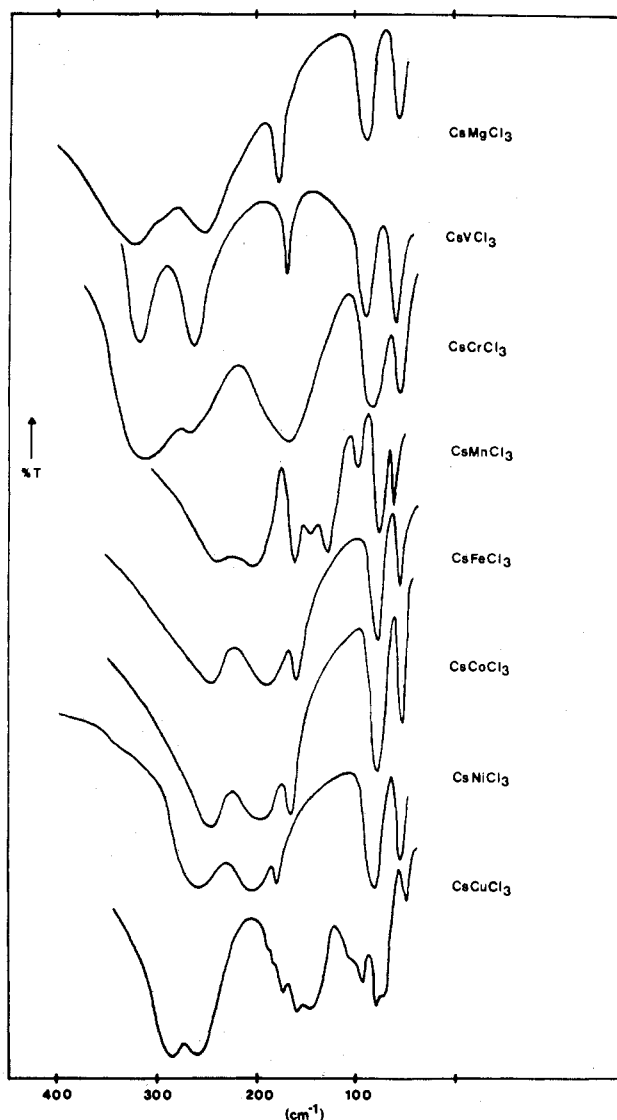


Figure 1. Low-frequency infrared spectra of the  $\text{CsM}^{II}\text{Cl}_3$  salts.

comparison of the spectra of  $\text{CsNiCl}_3$ ,  $\text{RbNiCl}_3$ , and  $\text{TlNiCl}_3$  indicates that changes in the cation have a relatively minor effect on the spectra of the  $M^I M^{II} X_3$  salts. The frequencies of the three higher energy bands are essentially the same in the spectra of the three salts. This is not surprising since these three bands,  $E_{1u}(a)$ ,  $A_{2u}(a)$ , and  $E_{1u}(b)$ , result from

metal-halogen vibrations which do not involve cation motions. The two lower energy bands,  $E_{1u}(c)$  and  $A_{2u}(b)$ , involve cation translations and appear at significantly lower frequencies in the spectrum of  $TiNiCl_3$  compared with those of the cesium and rubidium salts. On the other hand, changing the halogen affects the energies of all five active vibrations. In the spectra of  $CsNiI_3$ ,  $CsNiBr_3$ , and  $CsNiCl_3$ , the frequencies of corresponding bands increase in the order,  $I < Br < Cl$ , which is expected considering the masses of the different halide ions.

The frequencies of the internal vibrations of the  $M^{II}X_3$  anionic chain vary significantly from metal ion to metal ion. The frequencies of the three high-energy bands in the spectra of  $CsVCl_3$ ,  $(CH_3)_4NMnCl_3$ ,<sup>13</sup>  $CsFeCl_3$ ,  $CsCoCl_3$ , and  $CsNiCl_3$ , generally follow the trend, in order of increasing frequency,  $Mn < Fe < Co < Ni < V$ . (The three high-energy bands in the spectrum of  $(CH_3)_4NMnCl_3$  appear at 220, 170, and 148  $cm^{-1}$ .) Assuming that the small differences between the masses of the various metal ions do not strongly affect the vibrational frequencies within this series of compounds, the trend suggests that the force constants for the metal-halogen bonds follow the crystal field stabilization energies for the metal ions. For high-spin octahedral complexes the CFSE is at a maximum for the  $d^3$  and  $d^8$  configurations and is at a minimum for the  $d^5$  configuration. The  $d^3$ ,  $d^8$ , and  $d^5$  configurations correspond to the vanadium, nickel, and manganese salts, respectively.

**Registry No.**  $CsMgCl_3$ , 12371-11-8;  $CsVCl_3$ , 20959-74-4;  $CsCrCl_3$ , 13820-84-3;  $CsMnCl_3$ , 14219-53-5;  $CsFeCl_3$ , 15611-69-5;  $CsCoCl_3$ , 15305-74-5;  $CsNiCl_3$ , 15455-69-3;  $KNiCl_3$ , 15530-90-2;  $TiNiCl_3$ , 28480-14-0;  $RbNiCl_3$ , 18894-62-7;  $CsNiBr_3$ , 15455-70-6;  $CsMnBr_3$ , 36482-50-5;  $CsNiI_3$ , 38496-65-0;  $CsCuCl_3$ , 18437-47-3.

**Acknowledgment.** We gratefully acknowledge Tulane University for the support of this work.

(13) Including the manganese salt in these comparisons may not really be valid since the  $(CH_3)_4N^+$  ion is much larger than the  $Cs^+$  ion. The difference in cation size might lead to longer metal-halogen distances in  $(CH_3)_4NMnCl_3$ .

Contribution from the Institute of Inorganic Chemistry,  
University of Basel, CH-4056 Basel, Switzerland

### Ternary Complexes in Solution. XV.<sup>1</sup> Mixed-Ligand Copper(II) Complexes with 2,2'-Bipyridyl or 1,10-Phenanthroline and Pyrocatecholate or Derivatives Thereof

Helmut Sigel,\* Peter R. Huber, Rolf Griesser, and Bernhard Prijs

Received August 22, 1972

Systematic studies of mixed-ligand  $Cu^{2+}$  complexes revealed a surprisingly high stability of those ternary complexes formed by an aromatic amine and a second ligand with O as donor atoms.<sup>2</sup> For example, pyrocatecholate forms a more stable complex with  $Cu(bipy)^{2+}$  than with

$Cu(aq)^{2+}$ .<sup>3,4</sup> It was shown that one of the intrinsic factors governing the stability of these mixed-ligand complexes is the  $\pi$ -acceptor qualities of the amine.<sup>2</sup> From this point of view it is of interest to compare the stability of ternary complexes containing either 2,2'-bipyridyl or 1,10-phenanthroline and especially to see how large the expected stability increase with 1,10-phenanthroline actually is.<sup>5,6</sup>

Furthermore, there are several hints in the literature<sup>2,4,7</sup> that the  $\pi$  system of the ligand with O as donor atoms also has some influence on the stability of complexes and that, more important, "cooperative effects" may occur between the  $\pi$  systems of two ligands bound to the same  $Cu^{2+}$ . To test this hypothesis several derivatives of pyrocatecholate have been included in the present investigation. The stabilities of ternary complexes containing either 2,2'-bipyridyl or 1,10-phenanthroline and one of the following bidentate ligands with O as donors were determined: pyrocatechol (1,2-dihydroxybenzene), tiron (1,2-dihydroxybenzene-3,5-disulfonate), pyrogallol 1-methyl ether (1,2-dihydroxy-3-methoxybenzene), and 6,7-dihydroxy-naphthalene-2-sulfonate.

### Experimental Section

**Materials.** Tiron (disodium salt), pyrogallol 1-methyl ether, and 1,10-phenanthroline were purchased from Fluka AG, Buchs, Switzerland. 6,7-Dihydroxynaphthalene-2-sulfonate (sodium salt) was from Schuchardt, Munich. The other reagents were the same as used earlier.<sup>4</sup>

**Measurements and Determination of Constants.** The acidity constants,  $K_{HL}^H$ , of the ligands with hydroxy groups were determined<sup>8</sup> by adjusting a series of appropriate pH values of solutions ( $I = 0.1$ ,  $NaClO_4$ ;  $25^\circ$ ) containing these ligands and by recording the absorption spectra of these solutions with a Beckman DB Spectrophotometer connected with a W+W Electronic Hi-speed Recorder, Model 202. In the case of tiron the solutions were  $1.4 \times 10^{-4}$  M and the spectra were evaluated at 254, 278, and 330 nm; with pyrogallol 1-methyl ether (evaluation at 300 nm) and 6,7-dihydroxynaphthalene-2-sulfonate (evaluation at 244 and 266 nm) the concentrations were  $1.8 \times 10^{-4}$  and  $1.8 \times 10^{-5}$  M, respectively.

All the other constants were measured by potentiometric titrations ( $I = 0.1$ ,  $NaClO_4$ ;  $25^\circ$ ), carried out under  $N_2$  with 0.1 N NaOH (cf. ref 4). The stability constants of the binary and of the ternary complexes were computed as described previously.<sup>4,9-11</sup> The uncertainties given in the tables are 3 times the standard deviation.<sup>2</sup>

The acidity constants,  $K_{HL}^H$ , of 2,2'-bipyridyl and 1,10-phenanthroline and the stability constants of the corresponding

(3) G. A. L'Heureux and A. E. Martell, *J. Inorg. Nucl. Chem.*, **28**, 481 (1966).

(4) R. Griesser and H. Sigel, *Inorg. Chem.*, **9**, 1238 (1970).

(5) As 1,10-phenanthroline has  $\pi$ -acceptor qualities like 2,2'-bipyridyl,<sup>6</sup> an increase in stability must be expected for the corresponding ternary  $Cu^{2+}$  complexes.

(6) W. J. Eilbeck, F. Holmes, G. G. Phillips, and A. E. Underhill, *J. Chem. Soc. A*, 1161 (1967).

(7) F. A. Walker, H. Sigel, and D. B. McCormick, *Inorg. Chem.*, **11**, 2756 (1972).

(8) H. Sigel and H. Brintzinger, *Helv. Chim. Acta*, **47**, 1701 (1964).

(9) In the calculation of the stability constant,  $\beta_{Cu-Cu(Am)(OL)}$ , of the ternary complexes the following species were taken into account in all systems:<sup>10</sup> H,  $H_2(Am)$ ,  $H(Am)$ ,  $Am$ ,  $Cu(Am)$ ,  $Cu(Am)_2$ ,  $H_2(OL)$ ,  $H(OL)$ ,  $OL$ ,  $Cu(OL)$ ,  $Cu(OL)_2$ ,  $Cu$ ,  $Cu(Am)(OL)$ .<sup>4</sup> In the systems containing 1,10-phenanthroline (P) the species  $HP_2^+$  and  $HP_3^+$ , detected by Fahsel and Banks,<sup>11</sup> do not occur in significant concentrations under our experimental conditions:  $[Cu^{2+}]_{tot} = [P]_{tot} \leq 8 \times 10^{-4}$  M; the complex  $CuP^{2+}$  is formed for nearly 100% already at low pH values ( $pH > 2.5$ ). The species  $HP_2^+$  and  $HP_3^+$  are perceptible only at  $[P]_{free} > 10^{-3}$  M.<sup>11</sup> Additionally, calculations were carried out under the assumption that the formation of the copper(II)-amine 1:1 complex is complete; i.e., only the species  $Cu(Am)$ ,  $Cu(Am)(OL)$ ,  $H_2(OL)$ ,  $H(OL)$ ,  $OL$ , and H were taken into account. Still, the results obtained under this simplification are practically identical with those given in the tables (cf. also ref 1, 2, 4).

(10) Abbreviations: Am, amine; L, general ligand; OL, ligand with O as donor atoms. The coordinating forms of the ligands OL are the anions. Charges are omitted in all equations.

(11) M. J. Fahsel and C. V. Banks, *J. Amer. Chem. Soc.*, **88**, 878 (1966).

(1) Part XIV: P. R. Huber and H. Sigel, *Z. Naturforsch. B*, **27**, 1319 (1972).

(2) P. R. Huber, R. Griesser, and H. Sigel, *Inorg. Chem.*, **10**, 945 (1971).