

(OEt)Ph₂]₄}{BPh₄}, 42741-29-7; {IrH[P(OMe)₂Ph]₃}{BPh₄}, 42741-30-0; *trans*-{IrHCl[P(OMe)Ph₂]₃}{BPh₄}, 42741-31-1; *trans*-{IrHCl[P(OEt)₂Ph]₃}{BPh₄}, 42741-32-2; *cis*-{IrHCl[P(OEt)₂Ph]₃}{BPh₄}, 42741-33-3; *trans*-{IrHCl[P(OEt)Ph₂]₃}{BPh₄}, 42741-34-4; {Pd[P(OMe)Ph]₃}{BPh₄}, 42741-35-5; {Pd[P(OMe)₂Ph]₂}{BPh₄}, 42741-36-6; {Pt[P(OMe)₂Ph]₃}{BPh₄}, 42741-37-7; {Pt[P(OMe)Ph₂]₃}{BPh₄}, 42741-38-8; {Pt[P(OEt)₂Ph]₃}{BPh₄}, 42741-39-9; {Pt[P(OEt)Ph₂]₃}{BPh₄}, 42741-40-2; {Cu[P(OMe)Ph₂]₃}{BPh₄}, 42741-41-3; {Cu[P(OEt)Ph₂]₃}{BPh₄}, 42740-91-0; {Ag[P(OMe)₂Ph]₂}{BPh₄}, 42740-92-1; {Ag[P(OMe)Ph₂]₂}{BPh₄}, 42740-93-2; {Ag[P(OEt)₂Ph]₂}{BPh₄}, 42740-94-3; {Ag[P(OEt)Ph₂]₂}{BPh₄}, 42789-22-0; {Au[P(OMe)₂Ph]₂}{BPh₄}, 42740-85-2; {Au[P(OMe)Ph₂]₂}{BPh₄}, 42740-86-3; {Au[P(OEt)₂Ph]₂}{BPh₄}, 42740-87-4; {Au[P(OEt)Ph₂]₂}{BPh₄}, 42740-88-5; *trans*-{IrHCl[P(OMe)₂Ph]₃}⁺, 42740-95-4; *cis*-{IrH₂[P(OMe)Ph₂]₃}⁺, 42740-96-5; *trans*-{IrH₂[P(OEt)₂Ph]₃}⁺, 42740-97-6; *cis*-{IrH₂[P(OEt)₂Ph]₃}⁺, 42740-98-7; *cis*-{IrH₂[P(OEt)Ph₂]₃}⁺, 42740-99-8; *trans*-{IrH₂[P(OMe)₂Ph]₃}⁺, 42741-00-4; *cis*-{IrH₂[P(OMe)Ph₂]₃}⁺, 42741-01-5; *catena*-dibromo-(bicyclo[2.2.1]hepta-2,5-diene)ruthenium, 42740-81-8; *catena*-dichloro(bicyclo[2.2.1]hepta-2,5-diene)ruthenium, 42740-82-9; chlorohydridotris(triphenylphosphine)ruthenium, 19631-00-6; chloro-(carbonyl)bis(triphenylphosphine)iridium, 14871-41-1; di- μ -chloro-bis(cycloocta-1,5-diene)diiridium, 12112-67-3; hydrogen, 1333-74-0; di- μ -chloro-dichlorodihydrobis(cycloocta-1,5-diene)diiridium, 12148-12-8; dichloro(cycloocta-1,5-diene)palladium, 12107-56-1; dichloro(cycloocta-1,5-diene)platinum, 12080-32-9.

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Ternary Complexes in Solution. XVI.¹ Influence of the Size of the Chelate Rings on the Stability of Mixed-Ligand Copper(II) Complexes Containing Aliphatic Ligands

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The influence of the ring size on the stability of ternary Cu²⁺ complexes was studied (25°; $I = 0.1$). The differences, $\Delta \log K = \log K^{\text{CuA}_2\text{CuAB}} - \log K^{\text{CuB}_2}$, which correspond to the equilibrium $\text{CuA} + \text{CuB} \rightleftharpoons \text{CuAB} + \text{Cu}$, and the constants, $\log X$, concerning the equilibrium $\text{CuA}_2 + \text{CuB} \rightleftharpoons 2 \text{CuAB}$, were compared for aliphatic ligands forming five- and six-membered chelates: for A = ethylenediamine and B = oxalate ($\log X = 0.94$), glycinate (1.03), and 1,2-propylenediamine (0.31) (five membered) or malonate (2.31), β -alaninate (0.88), and 1,3-propylenediamine (1.00) (six membered); for A = 1,3-propylenediamine and B = oxalate (3.14), glycinate (2.37), ethylenediamine (1.00), and 1,2-propylenediamine (1.13) or malonate ($\log X = 2.55$) and β -alaninate (1.70). It is concluded that in general mixed ligand complexes containing a five- as well as a six-membered chelate ring are favored in comparison with those containing either two five- or two six-membered rings. Furthermore, it appears that ternary complexes containing two six-membered chelates are somewhat more stable than the corresponding complexes containing two five-membered rings. Additionally, two earlier results are confirmed: (i) if the formation of a ternary complex leads to a neutralization of charge, its formation is favored, and (ii) comparisons of mixed-ligand systems containing either ethylenediamine or 2,2'-bipyridyl reveal the stability increasing effect of the latter ligand and the discriminating qualities of the Cu²⁺-2,2'-bipyridyl 1:1 complex.

Systematic studies of mixed-ligand Cu²⁺ complexes reveal² that among the driving forces which lead to the formation of ternary Cu²⁺ complexes in solution are statistical factors,³⁻⁵ steric hindrance in one of the binary parent complexes,^{6,7} and neutralization of charge by forming the ternary complex.^{8,9} Ternary complexes of especially high stability are formed by an aromatic amine and a second ligand with O as donor atoms.^{1,10,11} The reason for this increased stability is due to cooperative effects and π -bond formation in these systems.^{11,12}

As the stability of binary chelate complexes is strongly de-

pendent upon the size of the ring,¹³ the same may be surmised for mixed-ligand complexes. In fact, this is confirmed by a recent study where one of the ligands was *aromatic*.¹⁴ These systems contained either two five-membered chelate rings or one five- and one six-membered ring. For the sake of an unequivocal generalization it is necessary to do a similar investigation with *aliphatic* ligands only. The ternary complexes studied now contain either two six-, a five- and a six-, or two five-membered rings. The stability constants of the following two series of complexes were determined or taken from earlier work: (i) the ethylenediamine-Cu²⁺-L system and (ii) the 1,3-propylenediamine-Cu²⁺-L system, where L = oxalate (ox) or malonate (mal), glycinate (gly) or β -alaninate (β -al), and ethylenediamine (en), 1,2-propylenediamine (1,2-prop), or 1,3-propylenediamine (1,3-prop).

Experimental Section

Materials. Ethylenediamine and glycine were from Fluka AG, Buchs, Switzerland. β -Alanine and 1,3-propylenediamine were obtained from the British Drug Houses, Ltd., Poole, England. Disodium oxalate or malonate were from Merck AG, Darmstadt, Germany. From ethylenediamine and 1,3-propylenediamine the respective dihydrochlorides were prepared. *Anal.* Calcd for C₂H₁₀N₂Cl₂ (en-2HCl): C, 18.06; H, 7.58; N, 21.06; Cl, 53.30. Found: C, 18.28; H, 7.76; N, 21.06; Cl, 53.29. *Anal.* Calcd for C₃H₁₂N₂Cl₂ (1,3-

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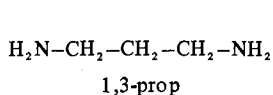
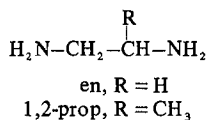
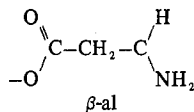
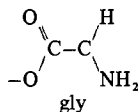
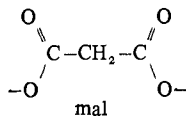
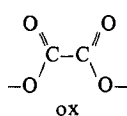
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Table I. Negative Logarithms of the Acidity Constants of the Ligands and Logarithms of the Stability Constants of Their Binary Cu²⁺ Complexes (*I* = 0.1; 25°)

L	pK ^H _{H₂L}	pK ^H _{HL}	Log K ^{Cu} _{CuL}	Log K ^{CuL} _{CuL₂}	Log β ^{Cu} _{CuL₂}
ox ¹⁶	1.37	3.81	4.84	3.6	8.44
gly ¹⁰	2.33	9.68	8.27	6.92	15.19
en ¹⁷	7.10	9.89	10.44	9.16	19.60
mal ¹⁰	2.62	5.30	5.10	2.55 ¹⁸	7.65
β-al ¹⁴	3.56	10.22	7.07	5.61	12.68
1,3-prop ¹⁴	8.85	10.62	9.82	7.22	17.04

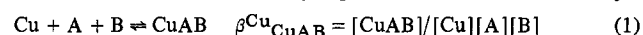


prop-2HCl): C, 24.50; H, 8.23; N, 19.05; Cl, 48.22. Found: C, 24.55; H, 8.20; N, 19.09; Cl, 48.10. The other substances were used as purchased. For all other materials see ref 10.

Measurements and Determination of Constants. All constants were measured by potentiometric pH titrations (25°; *I* = 0.1, NaClO₄) as described.¹⁰ The stability constant, $\beta^{\text{Cu}}_{\text{CuAB}}$, of the ternary systems was computed¹⁰ from the data obtained by alkalimetric titrations of solutions containing Cu²⁺ ([Cu(ClO₄)₂] = 6 × 10⁻⁴ M), amine dihydrochloride, and L in a ratio of 1:1:1, 1:2:1, 1:3:1, 1:4:1, 1:1:2, or 1:2:2 (with Cu-en-β-al additionally 1:1:4) and by taking into account the species H, H₂A, HA, A, CuA, CuA₂, H₂B, HB, B, CuB, CuB₂, Cu, and CuAB. The acidity constants of the ligands and the stability constants of the binary complexes used for the calculation of $\beta^{\text{Cu}}_{\text{CuAB}}$ were determined in earlier studies (cf. Table I).^{10,14,16-18} By titrating solutions containing Cu²⁺ alone, Cu:A = 1:1, or Cu:B = 1:1, it was proved that hydrolysis is negligible in the pH region used for the evaluation of the data.

Results

The results are assembled in Table II and the stability constants therein are defined by eq 1-3. The overall stability



constant of the ternary complex, log $\beta^{\text{Cu}}_{\text{CuAB}}$, is connected with the constants $K^{\text{CuA}}_{\text{CuAB}}$ and $K^{\text{CuB}}_{\text{CuBA}}$ by eq 4 and 5,

$$\log K^{\text{CuA}}_{\text{CuAB}} = \log \beta^{\text{Cu}}_{\text{CuAB}} - \log K^{\text{Cu}}_{\text{CuA}} \quad (4)$$

$$\log K^{\text{CuB}}_{\text{CuBA}} = \log \beta^{\text{Cu}}_{\text{CuAB}} - \log K^{\text{Cu}}_{\text{CuB}} \quad (5)$$

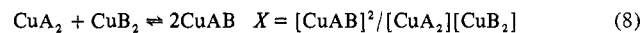
respectively.¹⁵

There are two convenient ways to characterize the stability of mixed-ligand complexes. One is according to eq 6, *i.e.*,

$$\Delta \log K = \log K^{\text{CuA}}_{\text{CuAB}} - \log K^{\text{Cu}}_{\text{CuB}} = \log K^{\text{CuB}}_{\text{CuBA}} - \log K^{\text{Cu}}_{\text{CuA}} \quad (6)$$

by comparing the difference in stability, $\Delta \log K$, *e.g.*, for the reaction between CuA or Cu(aq)²⁺ and the ligand, B. In addition, $\Delta \log K$ is identical with the constant due to

equilibrium 7. The other method is based on the "disproportionation" constant, log *X*, as defined by equilibrium 8 (calculated with eq 9 or 10). Generally, one would expect



$$\log X = 2 \log \beta^{\text{Cu}}_{\text{CuAB}} - (\log \beta^{\text{Cu}}_{\text{CuA}_2} + \log \beta^{\text{Cu}}_{\text{CuB}_2}) \quad (9)$$

$$\log X = (\log K^{\text{CuA}}_{\text{CuAB}} - \log K^{\text{CuB}}_{\text{CuB}_2}) + (\log K^{\text{CuB}}_{\text{CuBA}} - \log K^{\text{CuA}}_{\text{CuA}_2}) \quad (10)$$

to observe negative values for $\Delta \log K$ (eq 6), since usually it holds that $K^{\text{Cu}}_{\text{CuL}} > K^{\text{CuL}}_{\text{CuL}_2}$ (cf. Table I). The value expected for *X* (eq 8) on statistical reasons is 4, *i.e.*, log *X* = 0.6.^{3,4}

By using the results of Tables I and II, the values for $\Delta \log K$ (eq 6) and log *X* (eq 9) were calculated. The data are listed in Table III. To our knowledge, only the ethylenediamine-Cu²⁺-oxalate system had already been studied for which, under somewhat different conditions, the following values of log *X* had been determined: 1.4,¹⁹ 1.3,⁸ 1.1,⁴ and 1.0.³

Discussion

Within a pair of the systems, *e.g.*, ox-Cu-en and ox-Cu-1,3-prop, the binding sites are of the same kind, the only difference being the size of the chelate rings. Therefore, the results due to log $K^{\text{CuL}}_{\text{CuL(en)}}$ and log $K^{\text{CuL}}_{\text{CuL(1,3-prop)}}$ (cf., the right-hand columns in Table II) demonstrate the following. The addition of a second ligand forming a five-membered chelate to a binary 1:1 complex is favored over the coordination of a ligand forming a six-membered chelate (despite the fact that en is less basic than 1,3-prop) for all the given systems independent of the size of the chelate ring in the binary 1:1 complex. Hence, this result corresponds with the observations made by Irving, *et al.*,¹³ using binary complexes.

However, a comparison of the values due to log *X* (Table III) reveals that overall, ternary complexes containing a five- and a six-membered chelate are favored over the corresponding ones which contain two five-membered rings.²⁰ Similarly, it appears that in general (despite some exceptions) mixed-ligand complexes containing a five- and a six-membered ring are more stable than those formed by two six-membered rings. These facts are the result of the usually larger difference,²¹ log $K^{\text{Cu}}_{\text{CuL}} - \log K^{\text{CuL}}_{\text{CuL}_2}$, for the binary complexes with six-membered rings compared with this difference for the five-membered complexes (cf. Table I). There is only one exception, namely the six-membered binary Cu-β-al system; in this case the difference is in the order of the five-membered chelates, and indeed the log *X* value of en-Cu-β-

(15) Abbreviations: L, A, or B, general bidentate ligand. Charges are omitted in all equations.

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(20) The methyl group present in en-Cu-1,2-prop exhibits no significant steric influence, as a comparison of the data due to 1,3-prop-Cu-en and 1,3-prop-Cu-1,2-prop shows. Additionally, the above result confirms the one mentioned earlier, which was obtained with aromatic ligands.¹⁴

(21) This difference manifests itself indirectly in eq 10.

Table II. Logarithms of Stability Constants of the Ternary Cu^{2+} Complexes ($I = 0.1$; 25°)^a

Ethylenediamine- Cu^{2+} -L Systems				
Ring size	L	$\log \beta_{\text{Cu(en)L}}$	$\log K_{\text{Cu(en)}_{\text{Cu(en)L}}}$	$\log K_{\text{CuL}_{\text{CuL(en)}}$
Five	ox	14.49 ± 0.13	4.05	9.65
	gly	17.91 ± 0.13	7.47	9.64
	1,2-prop ^{b-d}	19.90	9.37	9.27
Six	mal	14.78 ± 0.14	4.34	9.68
	β -al	16.58 ± 0.20	6.14	9.51
	1,3-prop ^{b,c,e}	18.71	8.18	9.04

1,3-Propylenediamine- Cu^{2+} -L Systems				
Ring size	L	$\log \beta_{\text{Cu(prop)L}}$	$\log K_{\text{Cu(prop)}_{\text{Cu(prop)L}}}$	$\log K_{\text{CuL}_{\text{CuL(prop)}}$
Five	ox	14.31 ± 0.03	4.49	9.47
	gly	17.30 ± 0.02	7.48	9.03
	en ^{b,c,e}	18.71	9.04	8.18
	1,2-prop ^{b,d,e}	18.84	9.17	8.21
Six	mal	13.62 ± 0.09	3.80	8.52
	β -al	15.71 ± 0.05	5.89	8.64

^a The range of error given is three times the standard deviation. ^b These data were determined by graphical interpolation (for $I = 0.1$) from the results published by R. Nasanen and M. Koskinen, *Suom. Kemistilehti B*, 40, 108 (1967). ^c Cf. footnote b, en: $\text{p}K_{\text{H}_2\text{L}}^{\text{H}} = 7.06$, $\text{p}K_{\text{HL}}^{\text{H}} = 9.96$, $\log K_{\text{CuL}}^{\text{Cu}} = 10.53$, $\log \beta_{\text{CuL}_2}^{\text{Cu}} = 19.68$. ^d Cf. footnote b, 1,2-prop: $\text{p}K_{\text{H}_2\text{L}}^{\text{H}} = 6.85$, $\text{p}K_{\text{HL}}^{\text{H}} = 9.86$ (R. Nasanen, *Suom. Kemistilehti B*, 34, 4 (1961)), $\log K_{\text{CuL}}^{\text{Cu}} = 10.63$, $\log \beta_{\text{CuL}_2}^{\text{Cu}} = 19.81$. ^e Cf. footnote b, 1,3-prop: $\text{p}K_{\text{H}_2\text{L}}^{\text{H}} = 8.70$, $\text{p}K_{\text{HL}}^{\text{H}} = 10.54$, $\log K_{\text{CuL}}^{\text{Cu}} = 9.67$, $\log \beta_{\text{CuL}_2}^{\text{Cu}} = 16.74$.

Table III. Values of $\Delta \log K$ (eq 6) and $\log X$ (eq 9) of Some Ternary Cu^{2+} Complexes Containing Two Five-Membered or Two Six-Membered Chelate Rings or a Five- and a Six-Membered Chelate Ring ($I = 0.1$; 25°)

L	$\Delta \log K$	$\log X$	L	$\Delta \log K$	$\log X$
Ethylenediamine- Cu^{2+} -L Systems					
Five-, five-membered chelates			Five-, six-membered chelates		
ox	-0.79	0.94	mal	-0.76	2.31
gly	-0.80	1.03	β -al	-0.93	0.88
1,2-prop	-1.26	0.31	1,3-prop	-1.49	1.00
1,3-Propylenediamine- Cu^{2+} -L Systems					
Six-, six-membered chelates			Six-, five-membered chelates		
mal	-1.30	2.55	ox	-0.35	3.14
β -al	-1.18	1.70	gly	-0.79	2.37
			en	-1.49	1.00
			1,2-prop	-1.46	1.13

Table IV. Values of $\Delta \log K$ (eq 6) and $\log X$ (eq 9) of Some Ternary Cu^{2+} Complexes Containing Either the Aliphatic Amine, Ethylenediamine, or the Aromatic Amine, 2,2'-Bipyridyl ($I = 0.1$; 25°)

Ethylenediamine- Cu^{2+} -L			2,2'-Bipyridyl- Cu^{2+} -L		
L	$\Delta \log K$	$\log X$	L	$\Delta \log K$	$\log X$
ox	-0.79	0.94	ox ¹⁴	+0.7	4.9
gly	-0.80	1.03	gly ¹⁰	-0.35	3.05
1,2-prop	-1.26	0.31	en ¹⁰	-1.29	1.10
mal	-0.76	2.31	mal ¹⁰	+0.27	5.49
β -al	-0.93	0.88	β -al ¹⁴	-0.59	2.68
1,3-prop	-1.49	1.00	1,3-prop ¹⁴	-2.47	0.06

al is also similar to the one of en-Cu-gly while the one due to 1,3-prop-Cu- β -al is larger (Table III). Finally, a comparison of the $\log X$ values of the mixed five-five-membered chelates with the ones due to the six-six-membered chelates leads to the conclusion that for the latter ones equilibrium 8 is more strongly displaced toward the right side.

In Figure 1, the concentrations of the several complex species present in the systems 1,3-prop-Cu-ox and en-Cu-ox are shown in their dependence on pH. At higher pH values the concentration of the mixed complex dominates in both systems. The different magnitude of the stability constants due to the mixed-ligand complexes, as discussed in the last paragraphs, manifests itself unequivocally in the different formation degrees of the ternary species. The complex,

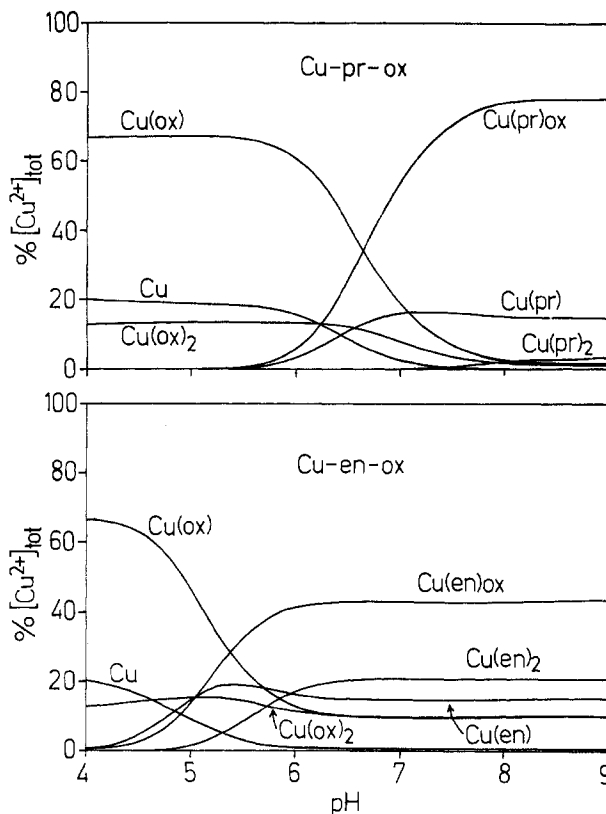


Figure 1. Variation with pH of the concentrations (given as the percentage of the total Cu^{2+} present) of the several species present in an aqueous solution of Cu^{2+} , oxalate (ox), and 1,3-propylenediamine (pr, upper part) or ethylenediamine (en, lower part); concentrations of the reactants, each 10^{-3} M. All data were computed with the constants given in Tables I and II. Hydrolysis was omitted in these calculations (cf. Experimental Section).

Cu(en)ox , reaches a maximum of 43% of the total Cu^{2+} present, while in the corresponding system the formation of Cu(1,3-prop)ox goes up to 78%.

Additionally, the results assembled in Table III confirm the earlier observation⁹ that neutralization of charge in the ternary complex, according to eq 11, favors their formation.



This means, the driving "forces" are coulombic attraction and a decrease in the orientation of the outer sphere solvent molecules (hence, enthalpy and entropy effects, respectively).

Finally, it is of interest to note that for all the systems listed in Table III the values for $\Delta \log K$ are negative, *i.e.*, equilibrium 7 is on its left side. This is obviously characteristic for ternary complexes containing an *aliphatic* amine and in contrast to those formed with *aromatic* amines.^{10,11} A more detailed comparison can be made based on the data listed in Table IV which are due to ethylenediamine-Cu²⁺-L systems and the corresponding 2,2'-bipyridyl-Cu²⁺-L systems. In fact, these results confirm unequivocally the earlier conclusion^{10,11} about the stability increasing effect of 2,2'-bipyridyl which was attributed to its π -accepting qualities.¹² As the data of $\Delta \log K$ and $\log X$ show, the mixed-ligand complex in the 2,2'-bipyridyl-Cu²⁺-L systems is always significantly more stable than the corresponding complex in the ethylenediamine-Cu²⁺-L system, as long as the second ligand, L, contains at least one oxygen atom as a donor.

Furthermore, the discriminating qualities of the binary Cu²⁺-2,2'-bipyridyl 1:1 complex are very remarkable; for example, the values of $\Delta \log K$ (*cf.* Table IV) differ for the 2,2'-bipyridyl-Cu²⁺-oxalate and the 2,2'-bipyridyl-Cu²⁺-ethylenediamine systems by about 2 log units, *i.e.*, a second ligand with oxygen donors is preferably bound. Compared with this result, the discriminating qualities of the Cu²⁺-ethylenediamine 1:1 complex are insignificant.

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Registry No. Ethylenediamine-Cu²⁺-ox, 21509-93-3; ethylenediamine-Cu²⁺-gly, 36960-82-4; ethylenediamine-Cu²⁺-1,2-prop, 16041-02-4; ethylenediamine-Cu²⁺-mal, 42934-35-0; ethylenediamine-Cu²⁺- β -al, 34178-70-6; ethylenediamine-Cu²⁺-1,3-prop, 16041-03-5; 1,3-propylenediamine-Cu²⁺-ox, 42934-38-3; 1,3-propylenediamine-Cu²⁺-gly, 42934-39-4; 1,3-propylenediamine-Cu²⁺-1,2-prop, 16041-04-6; 1,3-propylenediamine-Cu²⁺-mal, 42934-41-8; 1,3-propylenediamine-Cu²⁺- β -al, 42934-42-9.

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Infrared Intensity and Nuclear Magnetic Resonance Studies of Steric and Electronic Effects in (Pyrazolylborato)carbonyl Derivatives of Manganese(I)

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Infrared intensity studies of the carbonyl stretching vibrations in PzB(Pz)₃Mn(CO)₂L [Pz = 1-pyrazolyl; L = PCl₃, P(OC₆H₅)₃, P(C₆H₅)₃, P(*n*-C₄H₉)₃, P(C₆H₁₁)₃] and HB(CH₃PzCH₃)₃Mn(CO)₂P(OC₆H₅)₃ [CH₃PzCH₃ = 3,5-dimethyl-1-pyrazolyl] have been carried out. A method is proposed for determining the angles θ between CO vibrators in metal dicarbonyl compounds. Angles calculated for the pyrazolylborate derivatives indicate that the steric properties of the ligands influence the magnitude of the intercarbonyl angles. The electronic nature of the pyrazolylborate ligand is also compared with that of the cyclopentadienyl ligand. Nmr studies were carried out on the compounds PzB(Pz)₃Mn(CO)₂L [L = CO, P(OCH₃)₃, P(CH₃)₃] and HB(CH₃PzCH₃)₃Mn(CO)₂L [L = CO, P(OCH₃)₃, P(CH₃)₃, P(OC₆H₅)₃]. Whereas free rotation about the B-Mn axis occurred at 5° in the compounds PzB(Pz)₃Mn(CO)₂L and HB(CH₃PzCH₃)₃Mn(CO)₂L, stereochemical rigidity was observed in HB(CH₃PzCH₃)₃Mn(CO)₂L. Results are interpreted in terms of steric and electronic properties of the ligands.

Introduction

A number of substituted phosphine- and phosphite-dicarbonyl derivatives of the type PzB(Pz)₃Mn(CO)₂L [Pz = 1-pyrazolyl] and HB(CH₃PzCH₃)₃Mn(CO)₂L [CH₃PzCH₃ = 3,5-dimethyl-1-pyrazolyl] have been synthesized.² Steric properties of the ligand L were found to play an important role in the synthesis. However, no further investigation of the influence of steric effects on the structures of the compounds was reported. Furthermore, the electronic properties of pyrazolylborate ligands are not well understood. Since these tridentate, uninegative ions are analogous to the cyclopentadienide ion, it is of particular interest to compare electronic effects of PzB(Pz)₃Mn(CO)₂L with those of *h*⁵-C₅H₅Mn(CO)₂L.³ A comparison of carbonyl stretching frequencies

for the two series of compounds has been made previously,² but other physical measurements have not been reported.

The intensities of the carbonyl stretching vibrations in the infrared spectra of metal carbonyls have been proposed as a probe of electronic effects.⁴⁻⁸ Results of infrared intensity measurements on a variety of compounds of the type *h*⁵-C₅H₅Mn(CO)₂L have been interpreted in terms of the bonding properties of the cyclopentadienyl ligand.⁹ Attempts have also been made to use infrared intensities to determine angles in metal carbonyl derivatives.¹⁰⁻¹⁴ Most of the studies

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