The Carius tube was shaken for 2 hr and the solid was dissolved. The tube was opened and the solution was passed through a short 2-in. Florisil column, eluting with dichloromethane to give a clear colorless solution. The solvent was reduced in volume to about 2 ml and pentane was added to give white crystals. The flask was cooled at $-14°$ for 12 hr; then the solvent was decanted and the crystals were dried under vacuum; yield 80%.

Analogous complexes were prepared for the other acetylenes, using essentially the same procedure except that for involatile acetylenes, it was not necessary to conduct the reaction in a sealed Carius tube. Typical yields of the complexes are as follows: dimethyl acetylenedicarboxylate, 78%; 3,3,3-trifluoropropyne, 74%; diphenylacetylene, 82%; $C_6H_5C\equiv CCOOCH_3$, 83%.

(d) **Preparation of** *trans*-[Pt(CH$_3$){As(CH$_3$)$_3$}$_2$(N$_2$C$_3$H$_4$)](PF$_6$). To a solution of *trans*-Pt(CH$_3$)Cl{As(CH$_3$)$_3$}$_2$[41] (0.204 g) in 5 ml of acetone was added 0.106 g of silver hexafluorophosphate. The precipitated silver chloride was removed by centrifuging the solution. Pyrazole (0.029 g) was added and the acetone was removed by rotary evaporation to give a clear colorless oil. The oil was dissolved in dichloromethane and ether was slowly added until the solution became cloudy. The sides of the flask were scratched with a spatula, initiating the formation of long colorless crystals. The mother liquors were decanted and the crystals were washed with ether and dried under vacuum. The yield was 88%, mp 154–156°. Nmr in CDCl$_3$: δ(Pt–

CH$_3$) 0.43, δ(As–CH$_3$) 1.24, ^3J(Pt–H) = 23.0, δ(N–H) 11.34, δ(3-H) 7.63, ^3J(Pt–H) = 7.0, δ(4-H) 6.53, δ(5-H) 7.75.

Anal. Calcd for C$_{10}$H$_{25}$As$_2$F$_6$N$_2$PPt: C, 18.11; H, 3.80. Found: C, 18.03; H, 3.66.

Metal Complexes of the Three Sparteine Diastereoisomers. Properties and Reactivities of the Copper(II) Derivatives[1a-c]

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The natural alkaloid (–)-sparteine (C$_{15}$H$_{26}$N$_2$) and its two diastereoisomers, (–)-α-isosparteine and (–)-β-isosparteine, have been converted to crystalline copper(II) chloride complexes, whose properties are described. The evidence points to a tetrahedral environment about copper. Coordination with metal ions may be involved in the effect of sparteine upon muscle contraction.

Crystalline coordination compounds have been formed from copper(II) chloride and each of the three alkaloidal diastereoisomers (–)-β-isosparteine, (–)-sparteine, and (–)-α-isosparteine (Figure 1a, 1b, and 1c, respectively). Their structures and properties are described. At the time we had first isolated (–)-β-isosparteine from *Lupinus sericeus* Pursh and elucidated its structure and stereochemical relationship to the other isomers,[1b,c] we began the exploration of metal complexes derived from the sparteine stereoisomers. There had been a history of use of common (–)-sparteine as a reagent for qualitative cation analyses.[2]

Since the discovery of sparteine in 1850, the alkaloid has had a long history of use in medicine, particularly for the stimulation of muscular action in the heart,[3a] lung,[3b] and

uterus.[3c,4-6] As early as 1929[7] there were indications that some of the biological actions of sparteine may result from interactions with calcium ion *in vivo*. More recently, other studies[8,9] have shown that complexes of sparteine with organometallic compounds form in solution; some of these complexes have utility in directing stereoselective syntheses.

Recent progress[10,11] in the elucidation of the role of calcium ion in muscle contractile processes have caused us to take up again[12] the study of calcium complexes as possible inter-

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(1) (a) Contribution No. 2350 from the Department of Chemistry of Indiana University, Bloomington, Ind. 47401. (b) This is part III in a series; part I: M. Carmack, B. Douglas, E. W. Martin, and H. Suss, *J. Amer. Chem. Soc.*, 77, 4435 (1955). (c) Part II: M. Carmack, S. I. Goldberg, E. W. Martin, *J. Org. Chem.*, 32, 3045 (1967). (d) Paper presented before the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972; see Abstracts, No. INOR 67.

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(3) (a) E. L. McCawley in "The Alkaloids, Chemistry and Physiology," Vol. V. R. H. F. Manske, Ed., Academic Press, New York, N. Y., 1955, p 93; (b) M. J. Dallemagne and C. Heymans, *ibid.*, p 123; (c) A. K. Reynolds, *ibid.*, p 179.

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(10) (a) L. G. Welt and W. B. Blythe in "Pharmacological Basis of Therapeutics," L. S. Goodman and A. Gilman, Ed., 4th ed, Macmillan New York, N. Y., 1970, p 807; (b) A. L. Hodgkin, "The Conduction of the Nervous Impulse," Charles C. Thomas, Springfield, Ill., 1964, p 68.

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mediates in the effects of sparteine upon muscle action. Although we have apparently formed complexes with calcium salts, the products are difficult to characterize. The copper(II) complexes have, on the other hand, proved to be well suited for detailed structural investigation. While this paper was in revision, the publication by Mason and Peacock[13] describing a number of metal complexes with sparteine appeared; their compounds include the copper(II) chloride complex.

Of particular interest to us were the effects of the stereochemical variations[14] of sparteine upon the properties of the copper(II) complexes. This is mainly the effect of having the terminal A and D rings of the alkaloids folded in over the metal or folded out or a combination of both. In α-isosparteine (Figure 1, structure 1c), the A and D rings are more or less coplanar extensions of the B and C rings, extending beyond the two coordinating tertiary nitrogen atoms in such a way as to shield the metal atom from attack by reagent or solvent from two sides and also to hinder the possibility for two alkaloid molecules to coordinate simultaneously with one metal ion (a possibility which we attempted to realize preparatively). The β-isosparteine (1a) on the other hand has both A and D rings folded back in such a way as to allow the maximum exposure of the metal within the complex to attack by reagents or solvents. The possibility for coordination of two molecules of alkaloid with one of the metal ion appears from models to be most favorable in the β isomer, and we did indeed observe slight indications from color changes that such complexing may occur, but no crystalline adducts were isolated. The case of sparteine (1b), which has the A ring folded down over the metal and the D ring folded back away from the metal, is intermediate between the other isomers. It was found that these stereochemical differences are associated with differences in rates of hydrolysis: the doubly shielded α-isosparteine (1c) is the slowest hydrolyzing, the β-isosparteine copper(II) complex is the fastest, and the sparteine complex is intermediate.

Experimental Section

Materials. Anhydrous reagent grade methanol was distilled from calcium hydride. The (−)-sparteine was derived from commercial sparteine sulfate, $C_{15}H_{26}N_2 \cdot H_2SO_4 \cdot 5H_2O$, supplied by K & K Laboratories, Inc., Plainview, N. Y. 11803; it has the absolute stereochemical configuration shown in Figure 1.[1b,15] The β-isosparteine was supplied by M. C. from the earlier isolation from the plant *Lupinus sericeus* Pursh;[1b] it is identical with the base originally called spartalupine[1b,15] and is the (−) form having mirror-image relationship to the formula shown in Figure 1, 1a. The α-isosparteine was the (−) form derived by the procedure of Winterfeld and Rauch[16] from (−)-sparteine; its absolute configuration is represented in the third formula in Figure 1. ^{63}CuO (99.73% purity) and ^{65}CuO (99.70% purity) were purchased from Isotopes Development Center, Oak Ridge National Laboratories, Oak Ridge, Tenn. 37830.

Ligands. To avoid possible decomposition, all ligands were isolated just before reaction with metal salts. An aqueous solution of the salt was treated with excess KOH and the resulting oil extracted with ether, dried over $MgSO_4$, and then isolated in a Rotovac. The oil was then taken up in methanol.

pK_a Determination.[17] A 15-ml aqueous solution containing

(12) Both preparative work on complexes of the stereoisomers of sparteine with metal ions, including calcium ion, and pharmacological experiments on the mechanisms of action on muscle are projected.

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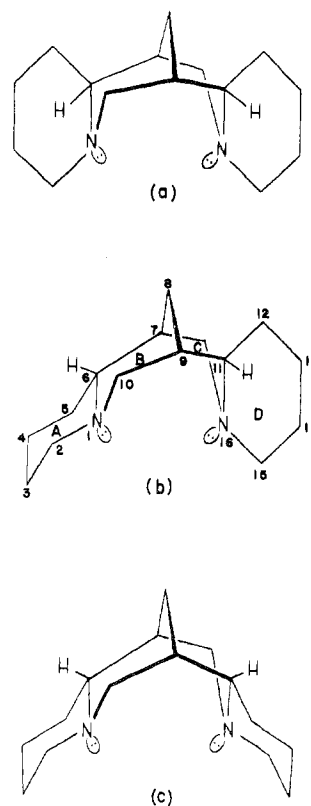(17) Unpublished data: E. F. Szymanski and M. Carmack, Chemistry Department, Indiana University, 1968.

Figure 1. Stereoisomers of sparteine: (a) (+)-β-isosparteine; (b) (−)-sparteine; (c) (−)-α-isosparteine.

the alkaloid diperchlorate (3×10^{-3} M) was titrated potentiometrically using a Beckman expanded-scale pH meter against 0.046 M tetraethylammonium hydroxide. The titrant was added from a microburet in increments of 0.05 ml for a total of some 32 readings. The pK_a values obtained at room temperature are as follows: α-isosparteine; pK_{a1} = 11.0, pK_{a2} = 3.5; sparteine; pK_{a1} = 10.8, pK_{a2} = 4.6; β-isosparteine, pK_{a1} = 10.8, pK_{a2} = 3.6.

Synthesis of Complexes. Copper(II) chloride complexes were prepared by mixing methanolic solutions of copper(II) chloride (previously dehydrated by heating at 110° for several hours) and the alkaloid oil in stoichiometric millimolar quantities. The green precipitates settled out immediately and were recrystallized from hot methanol.

The yellow-green β-isosparteine·$CuCl_2$ complex melted at 155–156° and decomposed at 180° (0.1 mm) yielding β-isosparteine; $[\alpha]^{25}$D +58° (in methanol). *Anal.* Calcd for $C_{15}H_{26}N_2CuCl_2$: C, 48.84; H, 7.12; N, 7.60; Cu, 17.22; Cl, 19.22. Found: C, 49.01; H, 7.28; N, 7.47; Cu, 16.87; Cl, 18.21.

The green sparteine·$CuCl_2$ complex melted at 160–161° and liberated sparteine at 200° (0.1 mm); $[\alpha]^{25}$D −112° (in methanol). *Anal.* Calcd for $C_{15}H_{26}N_2CuCl_2$: C, 48.84; H, 7.12; N, 7.60; Cu, 17.22; Cl, 19.22. Found: C, 48.64; H, 6.87; N, 7.89; Cu, 16.92; Cl, 18.81.

The blue-green α-isosparteine·$CuCl_2$ complex melted at 200° with decomposition and liberated α-isosparteine at 180° (5×10^{-5} mm). The optical rotation could not be measured owing to low solubility. *Anal.* Calcd for $C_{15}H_{26}N_2CuCl_2$: C, 48.84; H, 7.12; N, 7.60; Cu, 17.22; Cl, 19.22. Found: C, 48.23; H, 7.19; N, 7.69; Cu, 17.87; Cl, 19.18.

Copper isotope complexes of sparteine were prepared from ^{63}CuO and ^{65}CuO. One-half millimole of the oxide was first treated with excess hydrochloric acid, and the mixture was stirred and heated until complete solution was attained, whereupon excess HCl and water were removed by warming and evaporation. The solid cupric chloride was taken up in dry methanol and allowed to react with the alkaloid base in the usual manner described above.

The alkaloid:$CuCl_2$ ratio of 1:1 was confirmed by the method of continuous variations.[18] We hoped that it might be possible to obtain a complex, at least in the case of the β isomer, containing

(18) R. T. Pflaum and W. W. Brandt, *J. Amer. Chem. Soc.*, 76, 6215 (1954).

Table I. Hydrolyses Data for Sparteine Complexes at 25.0°

Complex	$10^3 k$, sec^{-1}	$t_{1/2}$, min
β-Isosparteine·CuCl$_2$	3.85	180
Sparteine·CuCl$_2$	2.62	264
α-Isoparteine·CuCl$_2$	2.35	295

two molecules of base to one of metal ion. No such compound was isolated in the present study.

Copper(II) bromide complexes were prepared by similar procedures.

Hydrolysis Studies. The rates of hydrolysis were determined by observing the disappearance of the alkaloid·CuCl$_2$ complex with a Spectronic 20 spectrophotometer. The reactions were followed at the wavelength maxima of 700 nm for β-isosparteine·CuCl$_2$ and sparteine·CuCl$_2$ and at 660 nm for α-isosparteine·CuCl$_2$. Concentrations of 1.0×10^{-3} M were used for the first two complexes, while solubility limitations set the concentration for α-isosparteine·CuCl$_2$ at 5.0×10^{-4} M. All solutions were thermostated in a constant-temperature bath at $25.0 \pm 0.1°$. Samples were removed and immediately centrifuged to remove any copper(II) hydroxide which might be present before absorbance readings were taken.

First-order hydrolysis constants were obtained from slopes of the straight-line portion of log (A_i/A_t) vs. time plots, where A_i and A_t are the absorbancies at the initial reading and at time t, respectively. A significant temperature dependency of the rate was observed; no systematic study of this variable was made.

Kinetic results for the hydrolysis reactions of the three isomeric complexes are given in Table I.

Spectra. The uv and visible spectra were recorded on a Cary Model 14 spectrophotometer with freshly prepared methanolic solutions ranging in concentration from 1.0×10^{-4} to 1.0×10^{-3} M. Near-infrared spectra (4000–670 cm^{-1}) were obtained on a Perkin-Elmer Model 137 sodium chloride spectrophotometer (Infracord) with KBr pellets for the solid samples and the neat ligand and oils between NaCl disks. Far-infrared spectra (600–200 cm^{-1}) were recorded on a Perkin-Elmer Model 621 spectrophotometer with Nujol mulls between polyethylene films and a FIS-3 spectrophotometer with KBr disks. The proton magnetic resonance spectrum of sparteine·CuCl$_2$ was checked with a Varian A-60A nmr spectrophotometer.

The disappearance of the distinctive spectra of the complexes was measured as a first-order reaction in dilute aqueous solutions to form the colorless alkaloid salts and liberate copper(II) ion or copper(II) hydroxide

alkaloid·CuCl$_2$ + 2H$_2$O = alkaloid·2H^{2+} + 2Cl^{2-} + Cu(OH)$_2$
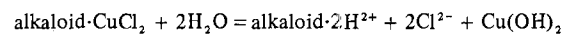
Results

Rates of Hydrolysis. Table I summarizes the first-order rate constants for disappearance of each of the isomeric copper(II) chloride complexes at 25.0° in dilute aqueous solution and also the half-lives in minutes.

Spectral Data. The electronic features of the spectra of the three complexes in methanolic solution are summarized in Table II and Figure 2. Table III gives the pertinent infrared data. As expected, no nmr absorptions were found for the complexes, an indication of the strong line-broadening effect of the paramagnetic d^9 system of copper(II).

Discussion

The X-ray crystallographic structure of α-isosparteine monohydrate[19] showed that all four rings of the alkaloid were in chair conformations. Although there is some evidence[20] that the C ring of free sparteine base may prefer a boat conformation, it appears likely that within the metal complexes all four rings are chairs. Bohlmann, *et al.*, have presented evidence[20a] that in β-isosparteine base the four rings have the all-chair conformation; it is a reasonable as-

(19) M. Przybylska and W. H. Barnes, *Acta Crystallogr.*, **6**, 377 (1953).

(20) (a) F. Bohlmann, D. Schumann, and C. Arndt, *Tetrahedron Lett.*, 2705 (1965); (b) M. Wiewiorowski and T. Skolik, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 11 (2), 69 (1963); (c) M. Wiewiorowski, O. E. Edwards, and M. D. Bratek-Wiewiorowska, *Can. J. Chem.*, **45**, 1447 (1967).

Table II. Electronic Spectral Data of Sparteine Complexes in Methanol

Complex	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
β-Isosparteine·CuCl$_2$	943	60.0
	825	99.5
	370 sh[a]	1960
	335	2200
	248	2128
Sparteine·CuCl$_2$	780	184.0
	355 sh	1880
	308	2180
	245	2368
α-Isosparteine·CuCl$_2$	949	81.6
	760	113.2
	321	2368
	242	1684

[a] sh = shoulder.
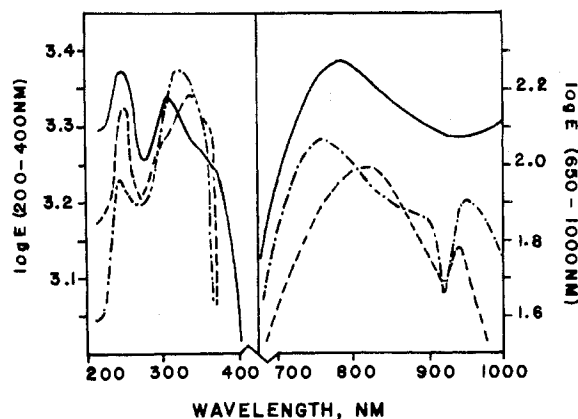
Figure 2. Electronic spectra in methanolic solution of: – – – –, β-isosparteine·CuCl$_2$; ———, sparteine·CuCl$_2$; – · – · –, α-isosparteine·CuCl$_2$.

sumption that the same is true of the metal complexes.[21]

Differences in optical properties, in thermal stabilities, and in reactivity toward water of the metal complexes in the situations thus far examined have always placed the three diastereoisomeric copper(II) complexes in ordered series in which sparteine is intermediate between the α and β forms. Since it is likely that all of the complexes exist in all-chair conformations, the most conspicuous differences are in the folding of the A and D rings, exposing to varying degrees the metal atom. More subtle differences resulting from bond lengths and/or bond angles may be revealed when X-ray crystallographic determinations are complete.[21] If the physical data, which tend to place sparteine in an intermediate position, may be extrapolated to biological phenomena, then there is a basis for hope that when complete pharmacological studies have been made on all the stereoisomeric alkaloidal forms, either the α or β isomers will show more intense biological responses than the sparteine isomer, with the A ring inclined endo and the D ring exo.

The d^9 electron configuration makes copper(II) would-be octahedral environments vulnerable toward Jahn–Teller distortions, which in extreme cases may lead to square arrangements. There is only a small barrier between square and tetrahedral configurations, which may be easily overcome by steric requirements placed by the ligand on the complex.[22] As a result, the geometrical arrangement about copper(II) is often not symmetrical and interpretations of its spectral

(21) The X-ray crystallographic structure determinations of the α- and β-isosparteine–copper(II) chloride complexes are currently being carried out by colleagues at Indiana University and will be reported separately.

(22) M. Elder and B. R. Penfold, *J. Chem. Soc. A*, 2556 (1969).

Table III. Infrared Data for Sparteine Ligands and Their Cupric Chloride Complexes

	Band position, cm⁻¹			
Compd	ν(N=CH)	ν(C–N)	ν(Cu–Cl)	ν(Cu–N)
β-Isosparteine	2890 s, 2840 sh, 2770 sh^a	1459 sh, 1435 s		
β-Isosparteine·CuCl₂	2992 s, 2900 s	1460 sh, 1440 s	282 s, 275 s	470 w, 448 w
Sparteine	2890 s, 2840 sh, 2740 s	1452 s, 1435 s		
Sparteine·CuCl₂	2900 sh, 2850 s	1430 s	297 s, 274 s	468 w, 436 w
α-Isosparteine	2924 s, 2850 sh, 2732 s	1473 s, 1449 s		
α-Isosparteine·CuCl₂	2945 s, 2870 w	1465 w, 1450 s	298 s, 285 s	478 w, 462 (?)

^{a} Key: s, strong; sh, shoulder; w, weak.

properties are therefore notoriously complicated. This appears to be the case for the cupric chloride–sparteine complexes. Nevertheless, the presence of several absorption bands indicates that the structure about the metal may not be perfectly tetrahedral.

The visible spectra show the usual unsymmetrical absorptions (likely due to several overlapping transitions) with the strongest maxima shifting from λ_{max} 825 nm for the light green β complex, to 780 nm for sparteine copper(II) chloride, to 760 nm for the dark green α complex.

Space-filling models show interligand repulsion to be very definite for the square arrangement. Furthermore, planar arrangements, due to their larger energy level splitting, absorb at higher energies (lower λ values) than tetrahedral arrangements[23] and the observed absorptions for sparteine complexes occur in the region typical for tetrahedral complexes. The low-energy shoulders are likely the result of Jahn–Teller distortion-induced ligand field stabilization energies, very much to be expected for tetrahedral copper(II).[24] The environment about copper in these complexes can thus be considered to be nearly tetrahedral (Figure 3), or at best distorted square planar.[13,25]

The infrared bands occurring in the 2800-cm⁻¹ region have been assigned to an interaction between the lone electron pairs of nitrogen and the electrons of neighboring C–H bonds.[26] From Table III it is seen that the absorptions in this region are definitely affected in going from the neat alkaloid to the corresponding complex. Similarly, the features of the C–N absorptions around 1450 cm⁻¹ also undergo changes upon metal complexation. Such shifts may be associated with the fact that in the complex the lone electron pair on nitrogen is tied up in the formation of a fairly rigid nitrogen–copper bond. While the perturbations of the 2800- and 1450-cm⁻¹ peaks are quite evident, no obvious trends may be detected.

To shed some additional light on the structures of these complexes and to identify the copper–ligand stretching vibrations we employed the metal isotope technique developed by Professor Nakamoto.[27] It allows the detection of small shifts in metal–ligand stretching frequencies when the spectra of two samples containing different isotopes of
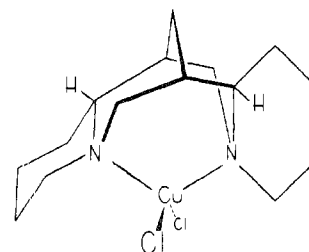

Figure 3. Proposed structure for sparteine·CuCl₂.

the same metal are compared in the far-infrared region. Only the vibrations involving the motions of the metal are shifted by metal isotope substitution.

Sparteine·CuCl₂ was chosen for the study of copper–ligand absorptions. The ⁶⁵Cu sample showed four small (1–3 cm⁻¹) but significant shifts to lower frequencies relative to the ⁶³Cu sample: two in the 280–300-cm⁻¹ region and two in the 440–480-cm⁻¹ region.

To identify the copper–chloride stretching frequencies we compared the far-infrared spectra of sparteine·CuCl₂ and β-isosparteine·CuCl₂ with the analogous bromide derivatives. In both cases it was found that the 280–300 cm⁻¹ absorption pair was lowered through bromide substitution by the predicted[28] factor of about 0.75. These two absorptions we have therefore assigned to Cu–Cl vibrations, while the high-frequency pair we assigned to the Cu–N vibrations. Metal–ligand vibrations for the other isomers (see Table III) were obtained by comparisons with the results from the sparteine isomer and should therefore be considered as tentative assignments.

Symmetry considerations[29] predict the number of infrared-active metal–ligand stretching bands for the two possible structures to be four (2 A₁ + B₁ + B₂ for tetrahedral C_{2v} and 2 A₁ + 2 B₁ for cis planar C_{2v} symmetry). Therefore no distinction can be made between the cis planar and tetrahedral structures by this method alone. Keeping in mind, however, stereochemical considerations and the results of electronic spectra discussed earlier, it may be concluded that the copper is in a nearly tetrahedral environment.[21]

(23) M. Manch and W. C. Fernelius, *J. Chem. Educ.*, **38**, 192 (1961).

(24) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3d ed, Interscience, New York, N. Y., 1972, pp 911–916.

(25) This conclusion has been substantiated simultaneously and independently by Mason and Peacock,[13] whose paper became known to us after our original manuscript had been completed.

(26) (a) F. Bohlmann, *Chem. Ber.*, **91**, 2157 (1958); (b) J. Skolik, P. J. Krueger, and M. Wiewiorowski, *Tetrahedron*, **24**, 5439 (1968).

(27) K. Nakamoto, *Angew. Chem., Int. Ed. Engl.*, **11**, 666 (1972).

(28) K. Nakamoto, "Infrared Spectroscopy of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., 1970, p 214.

(29) See ref 28, p 156, 208.