

tions with  $L = 3$  and  $M_l = 2$  are a completely suitable basis for the calculation. Inclusion of spin-orbit coupling removes the eightfold degeneracy and gives four doubly degenerate levels at  $3\lambda$ ,  $\lambda$ ,  $-\lambda$ , and  $-3\lambda$ . To simplify the calculation, the admixture of excited states with the ground state through spin-orbit coupling was neglected. The application of the Zeeman operators for the two unique directions yields the results given in Figure 9. The parallel and perpendicular

susceptibilities, according to the Van Vleck equation, are

$$\chi_{\parallel} = \left( \frac{N\beta^2}{kT} \right) \frac{25 + 9e^{2x} + e^{4x} + e^{6x}}{1 + e^{2x} + e^{4x} + e^{6x}}$$

$$\chi_{\perp} = \left( \frac{N\beta^2}{kT} \right) \left( \frac{1}{x} \right) \frac{-3 - e^{2x} + e^{4x} + 3e^{6x}}{1 + e^{2x} + e^{4x} + e^{6x}}$$

with  $x = \lambda/kT$ . Magnetic moments were calculated according to  $\mu_{\text{eff}} = (3kT/N\beta^2)^{1/2}(1/3\chi_{\parallel} + 2/3\chi_{\perp})^{1/2}$ .

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,  
ILLINOIS INSTITUTE OF TECHNOLOGY, CHICAGO, ILLINOIS 60616,  
AND TEXAS A&M UNIVERSITY, COLLEGE STATION, TEXAS 77843

## Halogenated Symmetrical Dipyrromethene Chelates<sup>1,2</sup>

BY R. J. MOTEKAITIS AND A. E. MARTELL<sup>3</sup>

Received February 11, 1970

A series of new chloro- and bromodipyrromethene chelates, synthesized by a novel metal ion exchange reaction, is described. These compounds were studied by nuclear magnetic resonance spectrometry and by infrared and electronic spectrophotometry. Physical and spectroscopic evidence are interpreted and correlated to deduce the microscopic structures of the Ca(II), Cu(II), Ni(II), Zn(II), and Mn(II) chelates with 3,3',4,4'-tetrachloro- and 3,3',4,4'-tetrabromo-5,5'-dicarbethoxy-2,2'-dipyrromethene ligands.

Dipyrromethenes have been known for many years and have been widely used as intermediates in porphyrin synthesis.<sup>4</sup> Their ability to form stable chelates with bivalent metal ions has also been described.<sup>4</sup> Since the initial work on these interesting chelate compounds comparatively few structural investigations have been reported. Porter<sup>5</sup> was the first to call attention to the exciting stereochemical problem caused by bulky substituents in the adjacent  $\alpha$  positions of different ligands coordinated to the same metal ion. Mellor and Lockwood<sup>6</sup> measured the magnetic moment of a Ni(II) chelate. West<sup>7</sup> investigated the exchange of radioactive Co(II) with a cobalt(II) dipyrromethenato chelate in pyridine solution. Corwin and Melville<sup>8</sup> studied the relative stabilities of metal chelates of porphyrins and dipyrromethenes. Eley and Spivey<sup>9</sup> measured the semiconductivities of several dipyrromethene chelates and concluded that there is some interaction between the  $\pi$  systems of ligands coordinated to the same metal ion. Ferguson, *et al.*,<sup>10,11</sup> studied

several bivalent metal chelates and on the basis of ligand field spectra, magnetic data, and X-ray powder photographs made conclusions favoring a general tendency toward tetrahedral configuration irrespective of the presence of  $\alpha$  substituents on the ligand. Murakami and Sakata<sup>12</sup> complemented this study with the inclusion of both near- and far-infrared spectral data as well as the calculation of Racah interelectronic repulsion integrals for these and similar systems.

The purpose of this work is to extend the relatively limited body of information available on dipyrromethene chelates. For the first time nuclear magnetic resonance (pmr) evidence is used in the elucidation of the structure of dipyrromethene chelates. This information is correlated with infrared and electronic spectra, followed by a discussion of heretofore unreported effects of the electronegative halo substituents on the ligands. Novel dipyrromethene chelates of a non-transition element ion, the Ca(II) ion, are described for the first time.

### Experimental Section

**General Data.**—Melting points were obtained with a Fisher-Johns melting point apparatus and are uncorrected. The microanalytical determinations were made by Alfred Bernhardt, Hobenweg, Germany. The proton magnetic resonance spectra were measured with a Varian Model A-60 spectrometer (tetramethylsilane internal standard;  $\tau$  units<sup>13</sup>). The solution infrared spectra were recorded with Spectrograde carbon tetrachloride as solvent in 0.10-mm sodium chloride cells on a Beckman Model IR-8 spectrophotometer calibrated with polystyrene film. The ultra-

(1) This work was supported in part by Research Grant GM11621 from the National Institute of General Medical Sciences, U. S. Public Health Service.

(2) Abstracted in part from a thesis submitted by R. J. Motekaitis to the faculty of the Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1967.

(3) To whom inquiries may be addressed: Texas A&M University, College Station, Texas 77843.

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TABLE I  
 MICROANALYTICAL DATA FOR DIPYRRROMETHENE CHELATES

| Formula  | % calcd |      |      |       |      | % found |      |      |       |      |
|--|---------|------|------|-------|------|---------|------|------|-------|------|
|  | C       | H    | N    | X     | M    | C       | H    | N    | X     | M    |
| C <sub>30</sub> H <sub>22</sub> N <sub>4</sub> Cl <sub>8</sub> O <sub>8</sub> Ca | 40.27   | 2.49 | 6.29 | 31.86 | 4.50 | 40.37   | 2.83 | 6.07 | 31.69 | 4.65 |
| C <sub>30</sub> H <sub>22</sub> N <sub>4</sub> Br <sub>8</sub> O <sub>8</sub> Ca | 28.92   | 1.78 | 4.50 | 51.31 | 3.22 | 28.89   | 1.82 | 4.28 | 51.40 | 3.38 |
| C <sub>30</sub> H <sub>22</sub> N <sub>4</sub> Cl <sub>8</sub> O <sub>8</sub> Cu | 39.43   | 2.43 | 6.13 | 31.04 | 6.95 | 38.92   | 2.45 | 6.16 | 30.59 | 6.33 |
| C <sub>30</sub> H <sub>22</sub> N <sub>4</sub> Br <sub>8</sub> O <sub>8</sub> Cu | 28.38   | 1.75 | 4.41 | 50.37 |      | 28.44   | 1.77 | 4.22 | 50.41 |      |
| C <sub>30</sub> H <sub>22</sub> N <sub>4</sub> Cl <sub>8</sub> O <sub>8</sub> Ni | 39.64   | 2.44 | 6.16 | 31.21 | 6.46 | 39.61   | 2.61 | 6.34 | 31.06 | 6.29 |
| C <sub>30</sub> H <sub>22</sub> N <sub>4</sub> Br <sub>8</sub> O <sub>8</sub> Ni | 28.49   | 1.75 |      | 50.56 |      | 28.35   | 1.86 |      | 50.72 |      |
| C <sub>30</sub> H <sub>22</sub> N <sub>4</sub> Cl <sub>8</sub> O <sub>8</sub> Zn | 39.35   | 2.42 | 6.12 | 30.98 |      | 39.97   | 2.45 | 6.07 | 30.72 |      |
| C <sub>30</sub> H <sub>22</sub> N <sub>4</sub> Br <sub>8</sub> O <sub>8</sub> Zn | 28.34   | 1.74 | 4.41 | 50.29 |      | 28.34   | 1.82 | 4.44 | 50.37 |      |
| C <sub>18</sub> H <sub>12</sub> N <sub>2</sub> Cl <sub>4</sub> O <sub>4</sub>    | 42.28   | 2.84 | 6.58 | 33.29 |      | 42.08   | 3.09 | 6.77 | 33.08 |      |
| C <sub>18</sub> H <sub>12</sub> N <sub>2</sub> Br <sub>4</sub> O <sub>4</sub>    | 29.82   | 2.00 | 4.64 | 52.93 |      | 29.94   | 2.20 | 4.87 | 52.93 |      |

violet and visible spectra were measured on a Cary Model 14 spectrophotometer with Spectrograde chloroform as solvent in 1-cm (0.997 cm by factory calibration) matched quartz cells. A Hitachi Perkin-Elmer vapor pressure osmometer was used to determine the molecular weights of the chelates in benzene. The calculated and measured values were identical within experimental error.

The deuteriochloroform used in pmr measurements was obtained from the Merck Chemical Co. Calcium oxide was N.F. grade. All other inorganic reagents and organic solvents used were of analytical grade and were obtained either from Baker or from Mallinckrodt.

**Bis(3,3',4,4'-tetrachloro-5,5'-dicarbethoxy-2,2'-dipyrrromethenato)calcium(II).**—A solution of 17.1 g of 3,3',4,4'-tetrachloro-5,5'-dicarbethoxy-2,2'-dipyrrylmethane<sup>14</sup> in 1500 ml of CCl<sub>4</sub> was boiled until all water had been removed. The cooled solution was then treated with 7.04 g of bromine in 25 ml of dry CCl<sub>4</sub> until all color was discharged (4 hr). To this solution was added 20 g of powdered calcium oxide and the mixture was vigorously shaken for 10 min. The intensely red solution was filtered and the solvent was removed under vacuum. The red-green residue was extracted (Soxhlet) into 2000 ml of hexane (24 hr). The residue from the extract was collected and combined with the crop obtained by concentrating the mother liquor; yield 10.6 g (59.8%).

**Bis(3,3',4,4'-tetrachloro-5,5'-dicarbethoxy-2,2'-dipyrrromethenato)copper(II).**—(Hereafter this will be called the standard procedure.) A hot solution of 1.002 g of copper(II) acetate monohydrate in 75 ml of glacial acetic acid was added to a hot solution of 4.270 g of bis(3,3',4,4'-tetrachloro-5,5'-dicarbethoxy-2,2'-dipyrrromethenato)calcium(II) in 175 ml of glacial acetic acid. The color of the solution became red. The open erlenmeyer was heated for an additional period (10 min). The solvent was removed under vacuum and the residue was extracted into 700 ml of hexane (24 hr). The crystalline material was collected and combined with additional crystals obtained from the mother liquor; yield 3.94 g (90%).

**Bis(3,3',4,4'-tetrachloro-5,5'-dicarbethoxy-2,2'-dipyrrromethenato)nickel(II).**—A mixture of 0.106 g of bis(3,3',4,4'-tetrachloro-5,5'-dicarbethoxy-2,2'-dipyrrromethenato)calcium(II) and 0.0311 g of nickel(II) acetate tetrahydrate was refluxed in 250 ml of absolute ethanol for 20 min. The product was worked up as in the standard procedure; yield 0.0443 g (41%).

**Bis(3,3',4,4'-tetrachloro-5,5'-dicarbethoxy-2,2'-dipyrrromethenato)zinc(II).**—A solution of 0.426 g of bis(3,3',4,4'-tetrachloro-5,5'-dicarbethoxy-2,2'-dipyrrromethenato)calcium(II) in 60 ml of dry tetrahydrofuran was treated with 0.110 g of zinc(II) acetate dihydrate and was heated to boiling for 10 min, and the residue was worked up as in the standard procedure; yield 0.123 g (28%).

**Bis(3,3',4,4'-tetrachloro-5,5'-dicarbethoxy-2,2'-dipyrrromethenato)manganese(II).**—A solution of 0.127 g of bis(3,3',4,4'-tetrachloro-5,5'-dicarbethoxy-2,2'-dipyrrromethenato)calcium(II) in 10 ml of glacial acetic acid was treated with 0.123 g of man-

ganese(II) acetate tetrahydrate; yield 0.0140 g (10.9%). This chelate is very sensitive to moisture.

**Bis(3,3',4,4'-tetrabromo-5,5'-dicarbethoxy-2,2'-dipyrrromethenato)calcium(II).**—A suspension of 5.27 g of 3,3',4,4'-tetrabromo-5,5'-dicarbethoxy-2,2'-dipyrrylmethane<sup>15</sup> in 400 ml of azeotropically dried carbon tetrachloride was treated with 1.40 g of bromine, followed by 10 g of calcium oxide according to the above preparation of the tetrachloro chelate of calcium(II); yield 3.69 g (73.8%).

**Bis(3,3',4,4'-tetrabromo-5,5'-dicarbethoxy-2,2'-dipyrrromethenato)copper(II).**—Following the standard procedure, a hot solution of 0.069 g of copper(II) acetate monohydrate in 10 ml of glacial acetic acid was poured into a hot solution of 0.264 g of bis(3,3',4,4'-tetrabromo-5,5'-dicarbethoxy-2,2'-dipyrrromethenato)calcium(II) in 20 ml of glacial acetic acid; yield 0.159 g (59%).

**Bis(3,3',4,4'-tetrabromo-5,5'-dicarbethoxy-2,2'-dipyrrromethenato)nickel(II).**—Similarly, 0.252 g of calcium chelate in 20 ml of acetic acid was treated with 0.088 g of nickel(II) acetate tetrahydrate dissolved in 10 ml of hot glacial acetic acid; yield 0.153 g (60%).

**Bis(3,3',4,4'-tetrabromo-5,5'-dicarbethoxy-2,2'-dipyrrromethenato)zinc(II).**—A hot solution of zinc acetate dihydrate in 50 ml of boiling tetrahydrofuran was added to a hot solution of 0.255 g of the bromodipyrrromethenato)calcium(II) chelate dissolved in 5 ml of tetrahydrofuran; yield 0.107 g (41%).

**3,3',4,4'-Tetrachloro-5,5'-dicarbethoxy-2,2'-dipyrrromethene and 3,3',4,4'-Tetrabromo-5,5'-dicarbethoxy-2,2'-dipyrrromethene.**—The ligands themselves were isolated as by-products from some of the lower yield chelate syntheses described above. They were recrystallized from hexane and were recovered as fine fluffy orange crystals.

## Results

**Synthesis.**—The new metal chelate compounds prepared in this study are represented by the general formula I, where X = Cl or Br and M = Ca(II), Cu(II), Ni(II), Zn(II), and Mn(II). Each ligand is shown in one of its two principal resonance forms. These chelates possess sharp melting points and definite sublimation temperatures. They melt to a red liquid and reversibly cool to a green solid. The crystals are dichroic; they are green but appear red when viewed against a bright light. When the crystals are pulverized, the product is red. The microanalytical data for these compounds are listed in Table I and their physical properties are summarized in Table II.

**Nmr Spectra.**—The nmr spectra of the new dipyrromethene chelates measured in deuteriochloroform are

(15) Prepared from ethyl 3,4-dibromo-5-methylpyrrolicarboxylate (H. Fischer, H. Beller, and A. Stern, *Chem. Ber.*, **61**, 1080 (1928)) by procedures outlined by R. J. Motekaitis, D. Heinert, and A. E. Martell, *J. Org. Chem.*, in press.

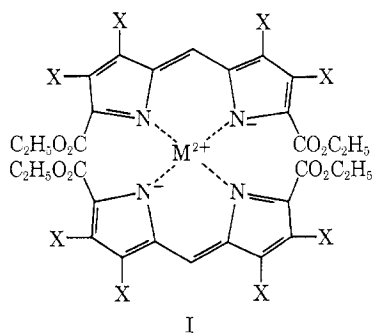
(14) H. Fischer and E. Elhardt, *Z. Physiol. Chem.*, **267**, 61 (1939).

TABLE II  
PHYSICAL CONSTANTS OF 3,3',4,4'-TETRAHALO-  
5,5'-DICARBETHOXY-2,2'-DIPYRROMETHENATO CHELATES

| Halogen | Metal ion | Subl pt, °C | Mp, °C               | Physical appearance            |
|---------|-----------|-------------|----------------------|--------------------------------|
| Cl      | Ca        | 275         | 286-287              | Light green square bipyramid   |
| Br      | Ca        | 275         | 303-304              | Light green square bipyramid   |
| Cl      | Cu        | 240         | 248-250              | Dark green needles             |
| Br      | Cu        | 257         | 263-265 <sup>a</sup> | Dark green needles             |
| Cl      | Ni        | 277         | 283-285              | Dark green needles             |
| Br      | Ni        | 291         | 299-300              | Dark green needles             |
| Cl      | Zn        | <i>b</i>    | 214-216              | Light green cubic              |
| Br      | Zn        | <i>b</i>    | 232-233              | Light green cubic              |
| Cl      | Mn        | <i>b</i>    | 218-220              | Light green crystalline solids |
| Cl      | H         | <i>c</i>    | 180-182 <sup>d</sup> | Orange filament-like crystals  |
| Br      | H         | <i>c</i>    | 225 <sup>d</sup>     | Orange filament-like crystals  |

<sup>a</sup> Melts followed by decomposition. <sup>b</sup> Sublimes above the melting point. <sup>c</sup> Does not sublime. <sup>d</sup> Decomposes.

presented in Table III. The ligand as well as the Ca(II) and Zn(II) chelates give rise to sharp spectra



consisting of the normal triplet-quartet pattern for the ethyl groups and a downfield singlet for the methine proton. Considerable structure is lost because of paramagnetic broadening in the remaining chelates (Mn(II), Ni(II), and Cu(II)); however the peaks still integrate in the expected ratio for the ethyl peaks. The Mn(II) compound shows a large paramagnetic shift to  $\tau$  7.8 (from  $\tau \sim 2$ ) and the Ni(II)-Br chelate shows even a larger one down to  $\tau$  15.0. The nickel(II)-chloromethine peak and the copper(II)-chloromethine and -bromomethine peaks could not be observed.

**Electronic Spectra.**—Both position and intensity of light absorption by these chelates in chloroform are recorded in Table IV. In the visible region each spectrum consists of three peaks: a low-intensity, rather broad band at 440–450  $m\mu$ , a medium-intensity, somewhat overlapping band at about 520  $m\mu$ , and a third relatively sharp peak of variable absorptivity at about 510–546  $m\mu$ . The latter peak is most intense with Ca(II), Zn(II), and Mn(II). However with Cu(II) and Ni(II) this peak appears at lower wavelengths with a concomitant loss in intensity.

In addition to the visible absorptions, there are in the ultraviolet region two closely spaced absorption bands: the first at about 260–270  $m\mu$  and the second

TABLE III  
NUCLEAR MAGNETIC RESONANCE SPECTRA OF  
5,5'-DICARBETHOXYDIPYRROMETHENE CHELATES

| Metal           | Halogen | Chem shifts <sup>a</sup> relative to tetramethylsilane in $\tau$ units | Bridge H      |
|-----------------|---------|--|---------------|
| H, -0.33, broad | Cl      | 8.57 (3), sharp<br>5.53 (4), sharp                                     | 2.73, sharp   |
| H               | Br      | 8.53 (3), sharp<br>5.53 (4), sharp                                     | 2.67, sharp   |
| Ca              | Cl      | 8.78 (3), sharp<br>5.80 (4), sharp                                     | 2.17, sharp   |
| Ca              | Br      | 8.78 (3), sharp<br>5.80 (4), sharp                                     | 2.28, sharp   |
| Zn              | Cl      | 8.87 (3), <sup>b</sup> sharp<br>5.97 (4), <sup>b</sup> sharp           | 2.28, sharp   |
| Zn              | Br      | 8.88 (3), sharp<br>5.97 (4), sharp                                     | 2.13, sharp   |
| Mn              | Cl      | 8.9 (30 Hz)<br>6 (150 Hz)  | 7.8 (50 Hz)   |
| Ni              | Cl      | 8.27 (10 Hz)<br>5.86 (30 Hz)   |               |
| Ni              | Br      | 8.27 (14 Hz)<br>5.88 (28 Hz)   | 15.00 (50 Hz) |
| Cu              | Cl      | 8.65 (20 Hz)<br>5.8 (140 Hz)   |               |
| Cu              | Br      | 8.57 (46 Hz)<br>6.1 (100 Hz)   |               |

<sup>a</sup> The number in parentheses following the chemical shift is the multiplicity if the band is split or the width at half-height if the band is broad. <sup>b</sup> The splitting constant for this ethyl group has been determined:  $J = 7.1 \pm 0.1$  Hz.

TABLE IV  
VISIBLE ABSORPTION SPECTRA OF 3,3',4,4'-TETRAHALO-  
5,5'-DICARBETHOXY-2,2'-DIPYRROMETHENATO  
CHELATES IN CHLOROFORM

| X <sup>a</sup> | M <sup>a</sup> | Wavelength, $m\mu$                   |                                      |                                      |
|----------------|----------------|--------------------------------------|--------------------------------------|--------------------------------------|
|                |                | $\lambda_{max}$ ( $\epsilon_{max}$ ) | $\lambda_{max}$ ( $\epsilon_{max}$ ) | $\lambda_{max}$ ( $\epsilon_{max}$ ) |
| Cl             | Ca             | 543 (179,000)                        | 520 (82,000)                         | 440 (12,000)                         |
| Br             | Ca             | 546 (204,000)                        | 520 (78,000)                         | 440 (10,000)                         |
| Cl             | Cu             | 504 (56,600)                         | <i>b</i>                             | 440 (19,000)                         |
| Br             | Cu             | 510 (72,600)                         | <i>b</i>                             | 445 (24,000)                         |
| Cl             | Ni             | 529 (75,300)                         | 500 (60,000)                         | 450 (18,000)                         |
| Br             | Ni             | 533 (90,000)                         | 510 (73,000)                         | 445 (17,000)                         |
| Cl             | Zn             | 537 (134,200)                        | 520 (95,000)                         | 450 (14,000)                         |
| Br             | Zn             | 541 (143,000)                        | 525 (125,000)                        | 450 (15,000)                         |
| Cl             | Mn             | 540 ( <i>c</i> )                     | 530 ( <i>c</i> )                     | 450 ( <i>c</i> )                     |
| Cl             | H              |                                      |                                      | 458 (18,600)                         |
| Br             | H              |                                      |                                      | 467 (20,000)                         |

<sup>a</sup> X, halo substituent; M, metal ion as in structure I. <sup>b</sup> Should appear but not possible to pinpoint position. <sup>c</sup> These extinction coefficients could not be determined accurately because of some solvolysis of chelate during measurement. Their relative ratios generally parallel those of Ca(II) and Zn(II) chelates and are 12.2:7.5:1.0.

about 3–8  $m\mu$  higher. Their molar absorbancies vary from 32,000 to 45,000 absorbance units. It was found that there are no more absorptions down to 210  $m\mu$  in *n*-hexane.

**Infrared Spectra.**—The dipyrromethene chelates with Ca(II), Mn(II), and Zn(II) show a single sharp carbonyl absorption at 1672–1730  $cm^{-1}$ . The Cu(II) and Ni(II) chelate spectra however have two bands: one at 1736–1751  $cm^{-1}$  and the second at 1642–1656  $cm^{-1}$ . All the chelates possess two carbon-carbon bond stretching absorptions at  $\sim 1600$  and at  $\sim 1480$   $cm^{-1}$ . The latter band may be a function of the halo-

gen substituent since it always appears at higher wave number in the chelates of the chloro-substituted ligands. These infrared absorptions are listed in Table V.

TABLE V  
INFRARED STRETCHING FREQUENCIES ( $\text{cm}^{-1}$ ) OF C=O AND C=C  
MODES OF BIS(3,3',4,4'-Tetrahalo-5,5'-dicarbethoxy-2,2'-  
dipyrromethenato)metal chelates in  
CARBON TETRACHLORIDE

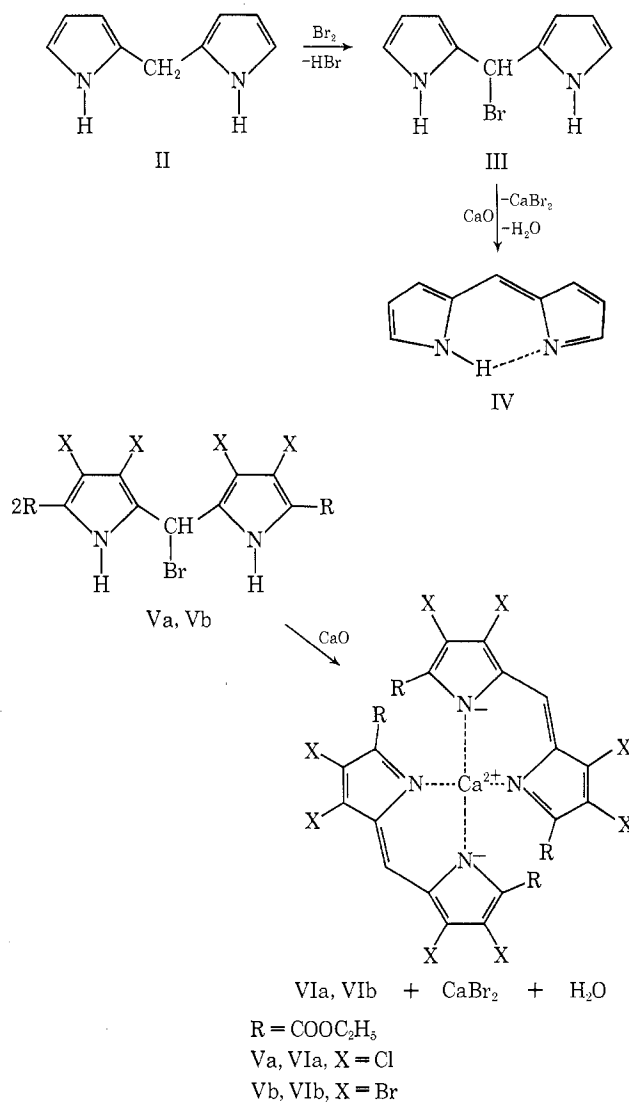
| Halogen | Metal          | C=O        | C=C        |
|---------|----------------|------------|------------|
| Cl      | Ca             | 1672       | 1592, 1488 |
| Br      | Ca             | 1669       | 1590, 1466 |
| Cl      | Mn             | 1695       | 1605, 1488 |
| Cl      | Zn             | 1730       | 1610, 1495 |
| Br      | Zn             | 1724       | 1605, 1473 |
| Cl      | Ni             | 1751, 1645 | 1605, 1493 |
| Br      | Ni             | 1748, 1642 | 1605, 1486 |
| Cl      | Cu             | 1736, 1650 | 1603, 1488 |
| Br      | Cu             | 1745, 1656 | 1608, 1475 |
| Cl      | H <sup>a</sup> | 1730, 1715 | 1618, 1477 |
| Br      | H <sup>a</sup> | 1730, 1715 | 1610, 1471 |

<sup>a</sup> The ligands are only sparingly soluble in  $\text{CCl}_4$ .

Other identifying bands are the methine C-H stretch at  $2994\text{ cm}^{-1}$  and ethyl C-H stretch at about  $2941\text{--}2950\text{ cm}^{-1}$ . The remaining 15 or so major peaks in these remarkably similar spectra could also be assigned empirically by comparison with pyrrole spectra and standard absorption charts. However, such assignments can be only tentative without a complete normal-coordinate analysis. In the fingerprint region of the spectrum only one prominent band seems to vary with halogen substitution. Curiously enough, it also varies with the central metal ion in an unusual way. Thus for calcium(II), zinc(II), and manganese(II) chloro chelates this strong band appears at  $1076$ ,  $1075$ , and  $1073\text{ cm}^{-1}$  whereas for the bromo chelates of Cu(II) and Zn(II) the band appears at lower frequencies ( $1065$  and  $1066\text{ cm}^{-1}$ ). For the nickel(II) and copper(II) chloro chelates the same band is at  $1056$  and  $1059\text{ cm}^{-1}$  and for Cu(II) and Ni(II) chelates of the bromo ligands it appears at  $1042\text{ cm}^{-1}$ . Although all spectra studied in this research have generally similar numbers and frequencies of ir absorption bands, the Ni(II) and Cu(II) spectra have several bands not present in the spectra of the Ca(II), Zn(II), and Mn(II) chelates, suggesting that the structures of these two groups of chelates may be somewhat different.

### Discussion

**General Data and Synthesis.**—One accepted method<sup>16,17</sup> for preparing dipyrromethene ligands involves initial oxidation (*i.e.*, substitution) by elemental bromine of the bridge methylene group of a dipyrromethane, II. The resulting dipyrrylmethyl bromide, III,<sup>18</sup> is then treated with either solid calcium oxide or hydroxide to remove hydrogen bromide in a hetero-



geneous neutralization-type reaction, to give the desired dipyrromethene base, IV, in excellent yield. However, in these laboratories the surprising result was observed that 3,3',4,4'-tetrachloro-5,5'-dicarbethoxy-2,2'-dipyrromethyl bromide, Va, and 3,3',4,4'-tetrabromo-5,5'-dicarbethoxy-2,2'-dipyrromethyl bromide, Vb, react with calcium oxide in carbon tetrachloride to form the corresponding soluble calcium(II) chelates, VIa and b. To prepare the Cu(II), Ni(II), Zn(II), and Mn(II) compounds advantage was taken of the relatively weak affinity of the  $\text{Ca}^{2+}$  ion for the nitrogen donor atoms of the ligand, and an exchange reaction was developed to replace this ion by transition metal ions. The Cu(II) and Ni(II) chelates were formed readily in acetic acid solution. Because exchange did not take place in acetic acid with Zn(II) and Mn(II), tetrahydrofuran was used instead for these two metal ions.

On the basis of an examination of their spectra and physical characteristics summarized in Table II, these metal chelates may be divided into two groups. Those of calcium(II), zinc(II), and manganese(II) crystallize from hexane in cubic or square-bipyramidal form, whereas those of copper(II) and nickel(II) crystallize as needles. The chelates of zinc(II) and manganese-

(16) H. Fischer and R. Nussler, *Justus Liebigs Ann. Chem.*, **491**, 167 (1931).

(17) K. Brunnings and A. Corwin, *J. Amer. Chem. Soc.*, **66**, 337 (1944).

(18) Depending on the substituents present, the product obtained upon brominating a less electronegatively substituted dipyrromethane could also be the isomeric dipyrromethene hydrobromide.<sup>17</sup>

(II) melt at lower temperatures than those of copper(II) and nickel(II). The melting point of the calcium(II) chelate is high compared to that of zinc(II) and manganese(II), probably because of greater ionic character exhibited by calcium(II) as a pretransition element.

**Nmr Spectra.**—The chelate I contains three types of protons: the methyl and methylene of the ester function and the bridgehead vinylic proton. The ethyl groups are expected to show a quartet and a triplet at  $\tau$  5.75 and 8.65 based on the spectra of halogenated pyrrole derivatives. The bridgehead resonance signal is estimated to be a singlet at  $\tau$  2.4–5.5.<sup>19</sup> The observed chemical shifts due to the ethyl group for the ligand are  $\tau$  5.53 and 8.57 for the chloro compound and  $\tau$  5.53 and 8.53 for the bromo compound. The methine proton shows a signal at  $\tau$  2.73 and 2.67 for the chloro and bromo ligands, respectively. Thus the chloro groups cause slightly greater shielding than the bromo groups in both the ethyl and the methine resonances.

For each substituent the differences of the nuclear magnetic resonance signals between the chelate and its respective ligand are tabulated in Table VI. A positive value means increased shielding and a negative value indicates deshielding relative to the ligand.

TABLE VI  
COMPARISON OF CHEMICAL SHIFTS ( $\tau$ ) OF SUBSTITUENT GROUPS IN BIS(3,3',4,4'-TETRAHALO-5,5'-DICARBETHOXYDIPYRROMETHENATO) CHELATES WITH THOSE OF THE FREE LIGAND

| M  | X  | $\Delta\tau(\text{CH}_2)$ | $\Delta\tau(\text{CH})$ | $\Delta\tau(\text{CH})$ |
|----|----|---------------------------|-------------------------|-------------------------|
| Ca | Cl | 0.21                      | 0.27                    | -0.56                   |
| Ca | Br | 0.25                      | 0.29                    | -0.39                   |
| Zn | Cl | 0.30                      | 0.42                    | -0.56                   |
| Zn | Br | 0.35                      | 0.44                    | -0.54                   |
| Mn | Cl | 0.3                       | 0.5                     | 5.1                     |
| Ni | Cl | -0.30                     | 0.33                    | ?                       |
| Ni | Br | -0.26                     | 0.35                    | 12.37                   |
| Cu | Cl | 0.08                      | 0.3                     | ?                       |
| Cu | Br | 0.04                      | 0.6                     | ?                       |

Upon chelation of the ligand with calcium(II) or zinc(II) the methine proton becomes deshielded and the ethyl protons become more shielded. In addition to the small perturbing effects caused by the metal, the relative position of the bridge protons is probably determined by the anisotropic diamagnetic effect of the carbonyl groups operating when the carboxyl oxygen atom is directed toward the bridge protons. Since each ethyl group is situated between two pyrrole groups of the other coordinated ligand, overall diamagnetic shielding of these protons occurs.

It has been observed<sup>20</sup> that in analogous 3,4-dihalo-pyrrole ethyl esters the methyl group is in general more influenced by the halogen than is the methylene group. Previous nmr studies<sup>20</sup> showed that in changing the halogen substituent from bromine to chlorine the resonance of the methyl group is shifted to a higher field a few parts per million more than is the signal of

the methylene group. In the present work, the chlorine also seems to cause a greater shielding effect on the methyl group than does the bromine substituent. In the metal chelates, the methylene group is closer to the halogen than is the methyl group. Molecular models indicate that the distance between the methylene group and the halogen is probably less than the distance between the methyl group and the two pyrroles of the ligand at right angles (the donor atoms of these ligands are arranged in a tetrahedral or distorted tetrahedral configuration, as discussed below). Thus greater shielding is postulated for the methylene by the chlorine, than for the methyl and methylene by the ring current of the opposite dipyrromethene group.

It can further be seen from Table III that the positions of the methyl resonance are the same for both halogens and that the positions of the methylene resonance are consistently higher for the bromo chelates than for the chloro chelates. These relative positions of ethyl resonances are reasonable in view of the increased ring current expected (in the chelates) in going from chlorine to the less electronegative bromine.

The ligand and the calcium(II) and zinc(II) chelates give very sharp spectra. The remaining chelates of manganese(II), nickel(II), and copper(II) give poorer spectra, with less resolution, and broad bands. The latter ions are paramagnetic and their chelates normally do not give nuclear magnetic resonance spectra. In the dipyrromethenato chelates, the ethyl groups are at sufficient distance from the metal in the spectra to be observed. The paramagnetic contact shifts<sup>21</sup> are apparently transferred through bonds (preferably double bonds) since the resonance position of the bridge proton is seen to be shifted to the greatest extent and the methyl group least, with the methylene groups showing shifts of intermediate magnitude. The resonance positions of the methine protons for the chloro-substituted Ni(II) chelate and both Cu(II) chelates could not be measured. These resonances were probably shifted downfield out of range of the instrument.

Although in this case nmr cannot provide positive proof of tetrahedral or distorted tetrahedral structures of dipyrromethene chelates, it can definitely be concluded that the Ca(II) and Zn(II) form diamagnetic and symmetrical chelates with both tetrahalodipyrromethene ligands, whereas Mn(II), Cu(II), and Ni(II) form paramagnetic chelates with these ligands.

**Electronic Spectra.**—Study of the electronic spectra in Table IV shows that the chelates of Ca(II), Zn(II), and Mn(II) differ from those of Ni(II) and Cu(II). The visible spectra of the chelates of the former group are characterized by larger extinction coefficients and longer wavelengths than those of the latter pair. The physical data of Table II are also in accord with establishing two groups of chelates for a given ligand. The fact that the Cu(II) and Ni(II) chelates each possess two carbonyl absorptions in the infrared provides the most conclusive evidence for establishing that Ca(II),

(19) R. Silverstein and G. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1963, p 82.

(20) R. J. Motekaitis, D. Heinert, and A. E. Martell, *J. Org. Chem.*, in press.

(21) D. Eaton and E. LaLancette, *J. Chem. Phys.*, **41**, 3534 (1964).

Zn(II), and Mn(II) chelates are quite different from those of Ni(II) and Cu(II).

Eley and Spivey<sup>9</sup> showed that there is some electronic interaction between the two dipyrromethene groups in Co(II) and Cu(II) chelates, while such interaction is absent in the corresponding Zn(II) complexes. Since the nature of this interaction was not made clear, a simple first-order perturbation-type resonance argument is presented here to infer the geometries of the chelates from electronic spectra.

Based on intensity and position, the longest wavelength absorption can be ascribed in simple MO theory to a  $V \leftarrow N$  type of transition whose relative position through the series of metal ions may be described in terms of the energy level diagram shown in Figure 1.

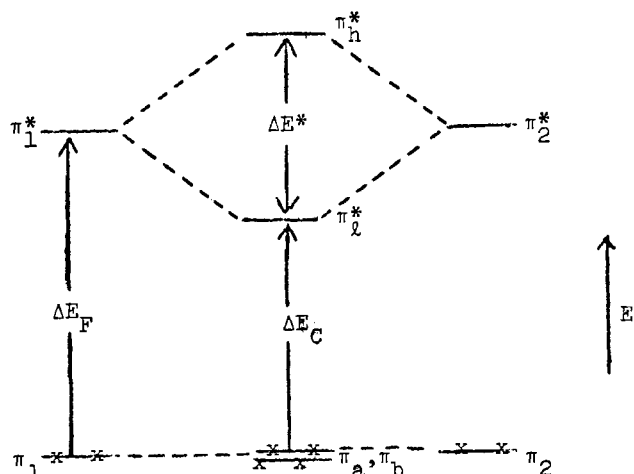


Figure 1.—Schematic energy level diagram depicting the energy changes of the lowest unoccupied excited MO's upon chelation of dipyrromethenes.

Here the two ligands are numbered 1 and 2. The highest occupied bonding MO's in the ground state prior to chelation are denoted by  $\pi_1$  and  $\pi_2$  while the lowest unoccupied excited MO's are  $\pi_1^*$  and  $\pi_2^*$ . Upon chelation, to a first approximation there is no overlap of the orthogonal  $\pi_1$  and  $\pi_2$  MO's. The resulting ground state MO's in the chelate are now indicated as  $\pi_a$  and  $\pi_b$ , a degenerate pair whose energy may be slightly lowered by mixing with metal orbitals. On the other hand, the lowest unoccupied orbitals  $\pi_1^*$  and  $\pi_2^*$  are not orthogonal and do interact upon chelation to produce two nondegenerate levels  $\pi_1^*$  and  $\pi_h^*$  with a net stabilized excited state. Thus, the absorption of the longest wavelength band in the free ligand corresponds to a  $\pi_1 \rightarrow \pi_1^*$  (or  $\pi_2 \rightarrow \pi_2^*$ ) transition with an energy of  $\Delta E_F$ . Similarly the longest wavelength transition in the chelate is  $\pi_a$  (or  $\pi_b$ )  $\rightarrow \pi_1^*$  with an energy of  $E_C$ .

If significant departure is made from tetrahedral toward square planar (rotation of  $\pi$  planes of opposite ligands from  $90^\circ$  to smaller angles), the overlap of the antibonding orbitals will decrease and  $\Delta E^*$  will shrink with a concomitant removal of degeneracy from  $\pi_a$  to  $\pi_b$ . The former effect is greater than the latter effect because the function  $\cos \theta$ , where  $\theta$  is the interplanar angle, changes more rapidly near  $90^\circ$  than

near  $0^\circ$ . The cosine behavior<sup>22</sup> of overlap and resonance integrals is well known. Thus in going from tetrahedral  $\theta = 90^\circ$  to square-planar  $\theta = 0^\circ$ , the energy of  $\pi_1^*$  increases more than does the ground-state  $\pi_a$  or  $\pi_b$ . Hence  $\Delta E_C$  becomes larger, and shorter wavelengths are expected when departure from regular tetrahedral configuration takes place.

Using this model, the chloro chelates may then be arranged on the basis of wavelength in the following order of deviation from tetrahedral configuration: Ca ( $543 \text{ m}\mu$ )  $\approx$  Mn ( $540 \text{ m}\mu$ )  $\approx$  Zn ( $537 \text{ m}\mu$ )  $<$  Ni ( $529 \text{ m}\mu$ )  $\ll$  Cu ( $504 \text{ m}\mu$ ). The same order is also inferred for the bromo chelates: Ca ( $546 \text{ m}\mu$ )  $\approx$  Zn ( $541 \text{ m}\mu$ )  $<$  Ni ( $533 \text{ m}\mu$ )  $\ll$  Cu ( $510 \text{ m}\mu$ ).

Band intensities, which are a measure of transition probability, may also be correlated with deviation from tetrahedral symmetry. Thus, the intensity of the longest wavelength band transition is assumed to follow the law

$$\frac{\epsilon^\theta}{\epsilon^{90}} = \sin^2 \theta$$

where  $\epsilon^{90}$  is the extinction coefficient of a reference compound known to be tetrahedral, *i.e.*,  $\theta = 90^\circ$ , and  $\epsilon^\theta$  is the extinction coefficient of a similar compound whose geometry is in question. This relationship is similar to that proposed by Braude and Sondheimer<sup>23</sup> to explain differences in intensities resulting from twisting of conjugated chromophores about a single bond. From Table VII which lists the results of these cal-

TABLE VII  
CORRELATION OF THE BAND INTENSITIES OF THE LONGEST WAVELENGTH ABSORPTION WITH INTERPLANAR ANGLES OF DIPYRROMETHENATO CHELATES

| Metal               | Chloro chelates                 |                 | Bromo chelates                  |                 |
|---------------------|---------------------------------|-----------------|---------------------------------|-----------------|
|                     | $\epsilon^\theta/\epsilon^{90}$ | $\theta$ , deg  | $\epsilon^\theta/\epsilon^{90}$ | $\theta$ , deg  |
| Ca(II) <sup>a</sup> | 1.33 <sup>a</sup>               | 90 <sup>a</sup> | 1.42 <sup>a</sup>               | 90 <sup>a</sup> |
| Zn(II) <sup>a</sup> | 1.0 <sup>a</sup>                | 90 <sup>a</sup> | 1.00 <sup>a</sup>               | 90 <sup>a</sup> |
| Ni(II)              | 0.56                            | 49              | 0.63                            | 52              |
| Cu(II)              | 0.42                            | 40              | 0.51                            | 45              |

<sup>a</sup> The calculation is based on the Zn(II) chelate as the known reference compound making the angle for the Ca(II) chelate too high; similar (slightly lower) values for  $\theta$  are obtained when Ca(II)-DPM is used as the standard tetrahedral chelate.

culations, it can be readily seen that the order of deviation from the tetrahedral angle is again found to be the same: Ca  $\approx$  Zn  $<$  Ni  $<$  Cu. The values in Table VII are only qualitative and should be considered in the light of the implied approximations, *i.e.*, (1) that the intensities of the bands are solely a function of the angle of twist between the planes, (2) that in going from one geometry to another the same selection rules hold for both limiting models, (3) that the molecular geometry of each ligand remains fixed and the symmetry of each ligand is constant, and (4) that the MO's of the tetrahedral and the theoretical square-planar configurations remain the same irrespective of the perturbations caused by each particular metal ion.

(22) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, Chapter 15.

(23) E. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).

A slight auxochromic shift was observed in the longest wavelength absorption peak in going from X = Cl to X = Br. In each case a hyperchromic effect was also observed. By taking ratios of intensities  $\epsilon_{\text{Br}}/\epsilon_{\text{Cl}}$ , the following order was obtained: ligand (1.1)  $\approx$  Ca (1.1)  $\approx$  Zn (1.1)  $<$  Ni (1.2)  $<$  Cu (1.3). From the values of  $\epsilon_{\text{Br}}/\epsilon_{\text{Cl}}$  (shown in parentheses) a correlation is evident between the proposed geometry of a given chelate and its ability to transmit electronegative effects. This observed correlation can be the result of several mechanisms. The bromo-substituted ligands are prone to greater polarizability and are more affected by metal ions that have greater tendencies toward covalency (toward planarity). A second explanation may be simply that of each pair of ligands with the same metal ion, the bromo chelate possesses a slightly larger interplanar angle (less deviation from the tetrahedral). Third, a strained geometry is expected to result in some distortion of ligand planarity. These mechanisms are a function of the geometries of the chelates and may operate in varying proportion depending on the extent of deviation from the tetrahedral.

The remaining two visible bands have already been described. However no immediate conclusions can be reached as to their origin since their intensities and exact positions cannot be precisely determined because of severe overlapping with each other. These bands are probably charge-transfer bands.

The two closely overlapping bands at about 270 m $\mu$  can be easily shown to be associated with the ester chromophore by the comparison in Table VIII of uv spectra of compounds VII-X.

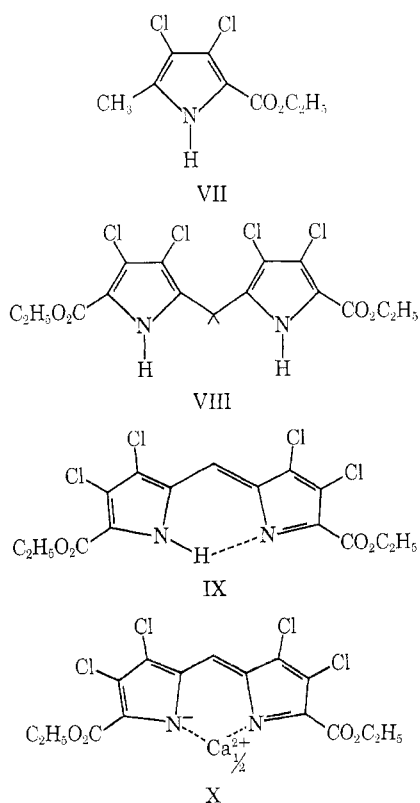
TABLE VIII  
UV ABSORPTION SPECTRA OF CARBETHOXY GROUP  
CONTAINING COMPOUNDS

| Compound | Band I  | Band II                                       |
|----------|---|---|
| VII      | 245 m $\mu$ ( $\epsilon$ 6950) <sup>a</sup>   | 275 m $\mu$ ( $\epsilon$ 15,440) <sup>a</sup> |
| VIII     | 247 m $\mu$ ( $\epsilon$ 14,000) <sup>a</sup> | 270 m $\mu$ ( $\epsilon$ 23,800) <sup>a</sup> |
| IX       | 257 m $\mu$ ( $\epsilon$ 17,000)              | 262 m $\mu$ ( $\epsilon$ 16,600)              |
| X        | 270 m $\mu$ ( $\epsilon$ 43,000)              | 277 m $\mu$ ( $\epsilon$ 47,200)              |

<sup>a</sup> From ref 20.

**Infrared Spectra.**—The ir spectra of all chelates studied are very much alike because the structures and most bond strengths are essentially invariant with substitution of metal and change of halogen. When both the halo group and the geometry remain constant and the metal ion is changed, only the M-N and possibly some N-C related absorptions will undergo appreciable shifts in position. If the geometry is varied (as in changing from a tetrahedral toward a distorted bipyramidal structure), then the additional vibrational spectral changes could be assigned only after a detailed mathematical analysis of force constants and the individual parts of the spectra they describe. The absence of significant changes in the ir spectra of the pyrrole ring and associated vibrations is an indication of the similarities of the basic ligand structures (*i.e.*, skeletal structures) of the compounds studied. The fact that the infrared spectrum is rather insensitive to such subtle changes resulting from change in halogen or metal ion is apparent from a consideration of the theory of group frequencies.<sup>24</sup> Even when the halo group is changed from Cl to Br, little secondary effect is seen on the ir spectrum of a given pyrrole.<sup>20</sup> The ir bands for which extensive shifts would be expected, that is, the C-Cl or C-Br stretching frequencies, could not be observed in the carbon tetrachloride solvent above 800 cm<sup>-1</sup>.

It is evident from Table V that the C=O stretching frequencies for Ca(II), Mn(II), and Zn(II) chelates are strong, sharp singlets and that their frequencies increase in the order Ca  $<$  Mn  $<$  Zn. For Ni(II) and Cu(II) chelates, this band is split into two equally intense singlets, one at a relatively high frequency and one at a relatively low one. From an examination of flexible models it becomes clear that upon twisting the tetrahedral model toward square planarity, the carbonyl of one carboxy group per ligand must deviate markedly from the plane of its ligand in order to minimize steric repulsions arising from the van der Waals contacts between the ethyl group and the opposite ligand. Therefore in departing from a tetrahedral arrangement toward a distorted square-planar structure, one carbonyl group progressively must twist out of its ligand plane with a loss of conjugation and its stretching frequency must rise. This prediction is borne out, as is clear from an examination of the C=O stretch data in Table V. The tetrahedral chelates (Ca(II), Mn(II), and Zn(II)) possess one C=O stretching mode and the distorted chelates (Ni(II) and Cu(II))



(24) L. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1962.

possess two peaks, one in the region of unconjugated esters and the other in the relatively low and usual position (*i.e.*, similar to that of the tetrahedral species).

A further examination of models of the tetrahedrally arranged chelates shows that a fully conjugated structure with the carbonyl group facing the metal ion is possible. This interaction ( $M \cdots O=C$ ) would be expected to lower the absorption frequency of the carbonyl to an increasing extent as the electropositive character of the metal ion increases. Calcium(II) is probably least shielded in this respect and a very low  $C=O$  ester frequency is therefore observed for the calcium chelate at  $1672\text{ cm}^{-1}$ . That this low frequency is in fact due to electrostatic metal ion carbonyl oxygen interaction is supported by the fact that the frequency of free ligand carbonyl is much higher (at  $1730\text{ cm}^{-1}$ ) than that of the calcium(II) chelate. The  $C=O$  frequencies of the remaining metal chelates are lowered to corresponding extents as the electrostatic interaction with the metal ion varies. In the Ni(II) and Cu(II) chelates, where the ester group is twisted from conjugation, this interaction is not possible, as is seen from the relatively high frequency of the corresponding bands.

Reference to Table V shows that there are two  $C=C$  stretching frequencies present in the ir spectra of halogenated dipyrromethenato chelates. The value of the first band in the spectra of halopyrroles<sup>20</sup> was fixed at  $1558 \pm 5\text{ cm}^{-1}$ . In dipyrromethenato chelates this value is some  $43\text{ cm}^{-1}$  higher, at  $1601 \pm 9\text{ cm}^{-1}$ . The second band at about  $1480\text{ cm}^{-1}$  is more variable and

is in about the same position as that for pyrroles.<sup>20</sup> The first band is seen to be more sensitive to electro-positive electron withdrawal by the  $M^{2+}$  ion. The second is more variant with the type of halogen than with the metal ion.

### Conclusions

It is seen that the information discussed above leads to the conclusion that the dipyrromethene chelates of this study fall into two groups: the tetrahedral Ca(II), Mn(II), and Zn(II) and the distorted tetrahedral Ni(II) and Cu(II). Previous workers have indicated preference for Ni(II) being regular tetrahedral and Cu(II) somewhat distorted. The present compounds differ from those previously reported by the presence of 12 strongly electron-withdrawing groups per metal chelate molecule (eight halo plus four carbethoxy groups per metal ion). These electronegative groups would tend to weaken the ligand field considerably around the central ion, producing a metal complex having overall greater ionic character in the metal-ligand bonds. The strong steric effects of the carbethoxy groups would also favor tetrahedral arrangement of the pyrrole nitrogen donor atoms. The fact that spectral data lead to the conclusion that deviations from tetrahedral structure are considerable and more than had been concluded for other dipyrromethene chelates is considered significant. These results suggest that the deviations from tetrahedral structure (toward coplanarity of the ligand planes) of the less substituted dipyrromethene chelates are perhaps greater than had previously been believed.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,  
UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER, BRITISH COLUMBIA, CANADA

## The Preparation and Characterization of Fluorocarbon-Bridged Di(tertiary phosphine and arsine) Complexes Derived from Triruthenium Dodecacarbonyl

BY W. R. CULLEN AND D. A. HARBOURNE

Received February 16, 1970

The reactions of triruthenium dodecacarbonyl with the fluorocarbon-bridged ligands ffars, ffos, and f<sub>6</sub>fos have been investigated under a variety of conditions. The complexes  $L_2Ru_3(CO)_8$  ( $L = \text{ffars}$  and  $\text{ffos}$ ),  $\text{ffars}Ru_3(CO)_{10}$ ,  $LRu_2(CO)_6$  ( $L = \text{ffars}$ ,  $\text{ffos}$ ,  $f_6\text{fos}$ ), and  $f_6\text{fos}Ru(CO)_3$  have been characterized. In addition, evidence for the existence of  $\text{ffos}Ru_3(CO)_{10}$  and  $\text{ffos}Ru(CO)_3$  is presented. The structures of these new compounds are discussed and compared with those of the corresponding iron derivatives.

Previous papers<sup>1-4</sup> have dealt with our investigation

(1) W. R. Cullen, P. S. Dhaliwal, and C. J. Stewart, *Inorg. Chem.*, **6**, 2256 (1967).

(2) (a) W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *J. Amer. Chem. Soc.*, **90**, 3293 (1968); (b) *Inorg. Chem.*, **8**, 95 (1969); (c) *ibid.*, **8**, 1464 (1969).

(3) W. R. Cullen, D. F. Dong, and J. A. J. Thompson, *Can. J. Chem.*, **47**, 4671 (1969).

(4) W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, **9**, 702 (1970).

into the complex-forming properties of the unsaturated

fluorocarbon-bridged ligands  $EC=CE(CF_2)_nCF_2$ : ffars,  $E = As(CH_3)_2$ ,  $n = 1$ ; ffos,  $E = P(C_6H_5)_2$ ,  $n = 1$ ; f<sub>6</sub>fos,  $E = P(C_6H_5)_2$ ,  $n = 2$ ; f<sub>3</sub>fos,  $E = P(C_6H_5)_2$ ,  $n = 3$ . In particular, novel complexes have been obtained from their reaction with iron carbonyls.<sup>2,4</sup> The aim of this present investigation was to extend the study