971. *Dipyrromethene Complexes of Transition Metals. Part I. Tetrahedral Complexes of Cobalt*(II), *Nickel*(II), *Copper*(II), *and Zinc*(II)

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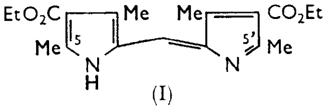
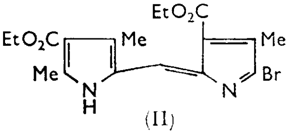
The complexes named in the title have been prepared with two different dipyrromethene ligands. Spectra, magnetic measurements, and *X*-ray powder photographs have been used to elucidate their stereochemistry.

COMPLEXES of transition metals with the bidentate ligand diethyl 3,3′,5,5′-tetramethyldipyrromethene-4,4′-dicarboxylate (I) have been known for some time.[1-3] These compounds, M(Ligand)$_2$, have been little studied, although their stereochemistry is interesting since the 5,5′-methyl groups prevent the two ligands bonded around the metal atom from achieving a square-planar configuration, especially with the bivalent metals nickel(II) and copper(II). It has been suggested that the cobalt, nickel, and copper complexes are tetrahedral,[2,3] and also that they are square-planar.[4,5]



(I)



(II)

We present new evidence, from spectra (Table 1), magnetic measurements (Table 2), and *X*-ray powder photographs, that the complexes of cobalt(II), nickel(II), and zinc(II) with diethyl 3,3′,5,5′-tetramethyldipyrromethene-4,4′-dicarboxylate (MMPM) (I) and diethyl 5′-bromo-3,4′,5-trimethyldipyrromethene-3′,4-dicarboxylate (MBrPM) (II) are tetrahedral. The copper complexes probably have a distorted tetrahedral arrangement.

The ligand-field bands of the cobalt complexes can be assigned to the transitions $^4A_2 \longrightarrow {}^4T_1(\mathrm{F})$, $^4A_2 \longrightarrow {}^4T_1(P)$ (band-splitting is probably due to spin–orbit coupling), in agreement with other assignments.[6] Solution and solid-state spectra are the same.

The magnetic moments of 4·3 and 4·53 B.M. for Co(MMPM)$_2$ and Co(MBrPM)$_2$, respectively, are in accord with the expected moments for tetrahedral cobalt(II) complexes (4·2—4·7 B.M.).[7] The values are lower than for an octahedral field because of less orbital contribution in the tetrahedral case.

Tetrahedral nickel(II) complexes are not common, but there is sufficient evidence[8-10] to enable us to say that the nickel–dipyrromethene complexes described are tetrahedral (see Tables 1a and 2). The ligand-field bands (the number, position, and intensity) can be interpreted on the basis of a tetrahedral model. Also, the bands are not shifted by a change of solvent (chloroform, ethanol, pyridine). In addition, Co(MBrPM)$_2$ and Ni(MBrPM)$_2$ are both isomorphous with Zn(MBrPM)$_2$, and Co(MMPM)$_2$ and Ni(MMPM)$_2$ are isomorphous.

The complexes formed with copper(II) are not isomorphous with the cobalt and nickel complexes, but they appear, from their *X*-ray powder photographs, to be structurally similar to the tetrahedral complexes. The high magnetic moments (2·28 and 2·13 B.M.) are in agreement with the predicted moment for a tetrahedral copper(II) complex.[11] The

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TABLE 1

(*a*) Ligand-field bands

Complex	ν (cm.$^{-1}$)	Molar extinction coeff.	Assignment
Co(MMPM)$_2$	9170sh		$^4A_2 \longrightarrow {}^4T_1(F)$
	10,260	54	
	13,830	187	$^4A_2 \longrightarrow {}^4T_1(P)$
	15,000	176	
Co(MBrPM)$_2$	9300sh		$^4A_2 \longrightarrow {}^4T_1(F)$
	10,400	55	
	13,010	498	$^4A_2 \longrightarrow {}^4T_1(P)$
	14,090	383	
Ni(MMPM)$_2$	6050	24	$^3T_1(F) \longrightarrow {}^3A_2$
	11,100	very weak	
	13,500	345	$^3T_1(F) \longrightarrow {}^3T_1(P)$
	14,600	337	
	15,750sh	shoulder	
Ni(MBrPM)$_2$	6450	26·9	$^3T_1(F) \longrightarrow {}^3A_2$
	12,310	645	$^3T_1(F) \longrightarrow {}^3T_1(P)$
	13,590	496	
	14,800sh	weak	
Cu(MMPM)$_2$	11,700	210	$^2T_2 \longrightarrow {}^2E$
Cu(MBrPM)$_2$	10,300	327	$^2T_2 \longrightarrow {}^2E$

(*b*) Charge-transfer bands

Complex	ν (cm.$^{-1}$)	Molar extinction coeff.	Complex	ν (cm.$^{-1}$)	Molar extinction coeff.
Co(MMPM)$_2$	16,950sh		Co(MBrPM)$_2$	16,680sh	
	17,390sh			17,220sh	
	18,200sh			19,210 *	1·53 × 10^5
	20,350 *	2·29 × 10^5		26,700?	
	27,800?			31,200sh	
	37,700	2·67 × 10^4		37,700	
Ni(MMPM)$_2$	15,750sh	(ligand-field?)	Ni(MBrPM)$_2$	14,800sh	(ligand-field?)
	20,200 *	0·97 × 10^5		18,200sh	
	21,750sh			19,050 *	6·8 × 10^4
	37,800	1·0 × 10^3		21,250sh	
	44,500?			31,000sh	
Cu(MMPM)$_2$	16,400sh			32,800sh	
	20,200 *	1·12 × 10^5		37,400sh	
	22,200 *	0·87 × 10^5		45,500sh	
	37,750	2·52 × 10^4	Cu(MBrPM)$_2$	15,610 *	2·25 × 10^3
	44,200?			18,700 *	9·37 × 10^4
MMPM	20,200sh			20,200 *	6·93 × 10^4
	22,200 *	8·7 × 10^4		32,200sh	
	37,750	4·0 × 10^4		37,050	
	45,500?		Zn(MBrPM)$_2$	19,300 *	1·71 × 10^5
MBrPM	16,690sh			20,400sh	
	20,200 *	4·4 × 10^4		32,100sh	
	21,050sh			37,800	
	32,800sh			45,500?	
	36,100	5·1 × 10^3			

* Bands probably similar to Soret band in porphyrins and metal–porphyrins.

TABLE 2

Magnetic susceptibilities

Compound	$\chi_g \times 10^6$ at 20°	μ (B.M.) at 20°	Expected value for tetrahedral field (20°)
Co(MMPM)$_2$	9·98	4·3	4·2—4·7
Co(MBrPM)$_2$	9·56	4·53	
Ni(MMPM)$_2$	6·14	3·42	3·5—4·2
Ni(MBrPM)$_2$	5·67	3·55	
Cu(MMPM)$_2$	2·42	2·28	2·0—2·2
Cu(MBrPM)$_2$	1·93	2·13	

reasonably high extinction coefficient of the ligand-field band is in agreement with a tetrahedral stereochemistry. However, the position of the ligand-field bands at 11,700 and 10,300 cm.$^{-1}$ for the two complexes appears to be too high unless the ligand exerts a very strong field. A similar problem has been discussed for the tetrahedral $CuBr_4^{2-}$ anion.[12] However, if the dipyrromethene complexes tend to be square-planar this would produce a strain on the ligand but would raise the energy of the ligand-field band.[12] The spectra of the co-ordinated ligands show considerable splitting of the charge-transfer band, associated with conjugation within the ligand at 20,000—22,000 cm.$^{-1}$ in the copper complexes. This may be indicative of the strain within the ligand. The spectra of the complexes are unaffected by change of solvent, which indicates that the co-ordination number has not been increased above 4. It appears from the above evidence that the copper complexes have a distorted tetrahedral configuration and a consequent strain of the ligand which is not so obvious in the other metal complexes.

The intense charge-transfer band of the free and co-ordinated ligands around 20,000—22,000 cm.$^{-1}$ is probably similar to the Soret band in porphyrins and metal–porphyrins,[13] which is said to be related to the conjugation or electron-delocalisation within the ligand. The band is shifted to longer wavelengths by electrophilic substituents and also by the co-ordinated metal atom. In the first case the electron-withdrawing group produces an increase in the electron-delocalisation. The effect of the metal will be similar in that the nitrogen atoms will become slightly positive, owing to co-ordination of the metal. This will again increase the electron-delocalisation, with a corresponding shift to longer wavelengths of the related absorption band.

EXPERIMENTAL

Carbon, hydrogen, and nitrogen were determined at the microanalytical laboratory, University of Otago, New Zealand.

Diethyl 3,3′,5,5′-*Tetramethyldipyrromethene*-4,4′-*dicarboxylate* (I).—This was prepared according to Mellor and Lockwood [3] (Found: C, 66·1; H, 7·1; N, 8·3. Calc. for $C_{19}H_{24}N_2O_4$: C, 66·3; H, 6·98; N, 8·14%).

Diethyl 5′-*Bromo*-3,4′,5-*trimethyldipyrromethene*-3′,4-*dicarboxylate* (II).—This was prepared according to Corwin and Viohl [14] (Found: C, 53·6; H, 5·8. Calc. for $C_{18}H_{21}BrN_2O_4$: C, 52·8; H, 5·14%).

Metal Complexes.—These were made by adding a warm concentrated solution of the ligand in ethanol and a concentrated soution of soldium acetate in water to a hot concentrated solution of the metal chloride in water. Excess of ligand was always employed. The dichroic green or red crystals of M(Ligand)$_2$ were recrystallised from ethanol.

		Found (%)					Required (%)			
Ligand	Metal	C	H	N	M	Formula	C	H	N	M
(I)	Co	60·6	6·5	8·9	—	$C_{38}H_{46}CoN_4O_8$	61·2	6·2	7·5	—
(I)	Ni	60·4	6·5	7·2	8·3	$C_{38}H_{46}N_4NiO_8$	61·2	6·2	7·5	7·9
(I)	Cu	59·8	6·4	7·4	—	$C_{38}H_{46}CuN_4O_8$	60·9	6·15	7·5	—
(II)	Co	50·1	5·1	5·5	—	$C_{36}H_{40}Br_2CoN_4O_8$	49·4	4·6	6·4	—
(II)	Ni	49·4	4·75	5·75	—	$C_{36}H_{40}Br_2N_4NiO_8$	49·2	4·6	6·4	—
(II)	Cu	48·7	4·8	5·7	—	$C_{36}H_{40}Br_2CuN_4O_8$	49·2	4·55	6·35	—
(II)	Zn	49·55	5·0	5·7	—	$C_{36}H_{40}Br_2N_4O_8Zn$	49·0	4·55	6·35	—

Physical Measurements.—Magnetic measurements were carried out at 20° by the Gouy method. Diamagnetic corrections were calculated by use of Pascal constants. Spectra were taken on a Beckman DK2A recording spectrophotometer. The solvents were chloroform, ethanol, and pyridine, and in each case the spectra were the same. The data in Table 1 are those recorded in chloroform.

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X-ray powder photographs were taken with a Phillips Debye–Scherrer camera using Cu K_α radiation. d-Values of the powder lines of certain of the complexes are:

Co(MMPM)$_2$ 10·24m, 8·88m, 7·46vw, 6·63s, 6·36w, 5·79m, 5·42m, 5·26w, 4·99w, 4·30w, 4·07w, 3·77m, 3·70w, 3·56s, 3·49w, 3·36w.

Cu(MMPM)$_2$ 11·29s, 9·00s, 8·17w, 7·79w, 7·34w, 6·63s, 5·80m, 5·50w, 5·24w, 5·02w, 4·67w, 4·21w, 3·73w, 3·64w, 3·51w.

Zn(MBrPM)$_2$ 10·03s, 9·26w, 7·52w, 6·94w, 6·45m, 6·09m, 5·26m—s, 4·72m—s, 4·51m—s, 3·85m, 3·71s, 3·20w, 3·11w, 2·81w, 2·61w, 2·48w.

Cu(MBrPM)$_2$ 8·09w, 7·19s, 6·59w, 6·09m—s, 5·65m—s, 5·32w, 4·99m—s, 4·87w, 4·59 diffuse—w, 4·43w, 3·77m—s, 3·57s, 3·39w, 2·68w.

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