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N-allylpyrazole as a Ligand. I. Preparation of Co(II), Cu(II), Zn(II), Cu(I) and Ag(I) Complexes

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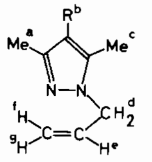
New complexes of allylpyrazole with metal ions have been prepared and characterized. The ir spectra of the monovalent metal complexes (Cu(I) and Ag(I)) indicate that the ligand is coordinated through both the pyrazolyl nitrogen and the olefinic group whereas divalent metal halides (Co(II), Cu(II) and Zn(II)) form 1 : 2 adducts with the ligand, in which only pyrazolyl nitrogen coordinates to the metal ion and the olefinic group is free. Cupric bromide reacts with allyldimethylpyrazole in ethanol and gives a cuprous complex by a novel type of reductive addition.

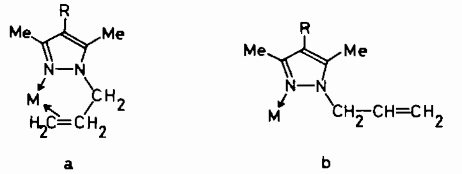
Introduction

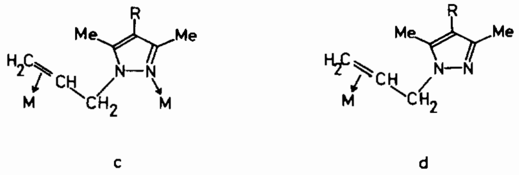
Allylpyrazole (I) is a new potential ligand containing two markedly different functional groups: a σ-donating nitrogen in the pyrazole ring and a π-bonding olefin in the allyl group.



I. N-allylpyrazole. R = H, CH_3. Small letters indicate positions of hydrogen atoms.

Hence, allylpyrazole should be able to participate in several types of coordination to metals (*e.g.* monodentate via either the pyrazolyl nitrogen or the olefin, or chelating and bridging bidentate coordination as shown in II).





II. Coordination modes of N-allylpyrazole.

The ligand may be expected to yield "stable" olefin complexes through the formation of unsymmetrical chelates.

Previously, the coordination chemistry of several phosphine–olefin and arsine–olefin ligand types have been reported[1], but for a nitrogen–olefin type ligand, only 2-allylpyridine[2] and allylamine[3] are known and have received limited attention.

In this work, the first of a series, the reactions of Cu(I), Ag(I) and divalent metal halides of the first transition period with allylpyrazole have been surveyed, and the isolated complexes have been spectroscopically characterized.

Experimental

Preparation of the Ligand and Complexes

1-Allyl-3,5-dimethylpyrazole (ADMP) and 1-allyl-3,4,5-trimethylpyrazole (ATMP)

The ligands were prepared according to Finar's method[4] in *ca.* 35% yield from 3,5-dimethylpyrazole or 3,4,5-trimethylpyrazole and allyl bromide in ethanolic potassium hydroxide solution. Both products were colourless viscous liquids.

Bis(1-allyl-3,5-dimethylpyrazole)metal(II) dihalide complexes: $MX_2(ADMP)_2$ (M = Co, Cu, Zn. X = Cl, Br)

The divalent metal halide was dissolved in ethanol and ADMP (2 mol) was added with stirring. The solution was heated at 80° C on the water bath for one hour, and then set aside at room temperature. The virtually quantitative yield of crystalline product was recrystallized from dichloromethane–n-hexane solution. All the complexes were soluble in acetone, chloroform and ethanol, but insoluble in benzene, ethyl ether and n-hexane. Elemental analyses and some physical properties are given in Table I. Attempts to prepare Mn(II) Fe(II) and Ni(II) complexes by this procedure were unsuccessful.

1-Allyl-3,5-dimethylpyrazole copper(I) halides: CuX(ADMP) (X = Cl, Br, I)

Cuprous complexes were synthesized in the manner used to prepare 2-allyl pyridine complex[2]. All the manipulation were carried out under a nitrogen atmosphere. CuX (0.01*M*), ADMP (0.01*M*) and Cu powder (0.2 g) were mixed in acetonitrile (20 ml) and stirred at room temperature. The white crystals which formed immediately were dissolved on heating. Copper powder was removed by hot filtration (yield *ca.* 70%) and the complexes containing cuprous chloride and cuprous bromide were recrystallized from ethanol. The cuprous iodide adduct was recrystallized from acetonitrile, because of its insolubility in most organic solvents. All complexes were colourless and diamagnetic, stable in air in the crystalline form but easily oxidized by air in solution. Elemental analyses and some physical properties are given in Table I.

1-Allyl-4-bromo-3,5-dimethylpyrazole copper(I) bromide: $CuBrC_8H_{11}N_2Br$

The reaction of $CuBr_2$ with ADMP in ethanol was carried out in the same way as for other divalent metal complexes. Colourless crystals (A) (yield *ca.* 40%) were, however, obtained from the ethanol solution. The product (A) was diamagnetic and the elemental analysis agreed with the total formula, $CuBr_2C_8H_{11}N_2$. Pyrolysis of (A) *in vacuo* yielded colourless liquid (B) and a white powder. The liquid (B) had elemental analysis $C_8H_{11}N_2Br$ (Found: C, 46.28; H, 5.09; N, 13.27. Calcd: C, 44.66; H, 5.15; N, 13.02%). Both (A) and (B) had no ^{1}H NMR signal corresponding to 4-H in the ring. Both exhibited π–π^* band maxima at 229 nm, compared with 221 nm for free ADMP. All these facts indicate that the product (A) was (1-allyl-4-bromo-3,5-dimethylpyrazole)cuprous bromide, $CuBr(C_8H_{11}N_2Br)$.

A mixture of cupric bromide and 1-allyl-3,4,5-trimethylpyrazole (ATMP) in which the 4-position of the ring was methylated to avoid the bromination, gave dark brown bis-pyrazolyl complex, $CuBr_2(ATMP)_2$. Cupric bromide reacted with 1-phenyl-3,5-dimethylpyrazole (PhDMP) to yield the cupric complex, $CuBr_2(PhDMP)_2$. Analytical data are given in Table I.

TABLE I. Elemental Analyses and Physical Properties of the Complexes.

Complex	Colour	M.p. (° C)	C	H	N	Metal	ν(C=C)
$CoCl_2(ADMP)_2$	Blue	130–131	47.50	5.90	13.94	14.83	1650
			(47.78)^a	(6.01)	(13.93)	(14.65)	
$CoBr_2(ADMP)_2$	Blue	125–127	39.23	4.76	11.53	11.77	1648
			(39.13)	(4.93)	(11.41)	(12.00)	
$CuCl_2(ADMP)_2$	Grey–green	109–110	47.22	5.83	13.64	15.41	1651
			(47.24)	(5.95)	(13.77)	(15.61)	
$ZnCl_2(ADMP)_2$	White	114–115	46.96	5.48	13.67	16.27	1649
			(47.02)	(5.92)	(13.71)	(16.00)	
$ZnBr_2(ADMP)_2$	White	131–133	38.56	4.74	11.34	13.20	1640
			(38.62)	(4.86)	(11.26)	(13.14)	
$CuBr_2(ATMP)_2$	Brown	104–106	41.56	5.32	10.45	12.67	1645
			(41.27)	(5.39)	(10.70)	(12.13)	
$CuBr_2(PhDMP)_2$	Brown	122	46.79	4.41	9.92	11.21	–
			(46.54)	(4.26)	(9.87)	(11.19)	
CuCl(ADMP)	White	117.5–118	40.90	5.03	11.78	26.93	1543
			(40.85)	(5.14)	(11.91)	(27.02)	
CuBr(ADMP)	White	109.5–111	34.38	4.16	10.02	22.75	1540
			(34.36)	(4.33)	(10.02)	(22.72)	
CuI(ADMP)	White	112–115	29.58	3.73	8.84	19.60	1545
			(29.42)	(3.70)	(8.58)	(19.45)	
CuBr(ADMPBr)	White	136–138	27.07	3.05	7.62	18.10	1542
			(26.80)	(3.09)	(7.81)	(17.72)	
$AgNO_3(ADMP)$	White	78–79	31.71	4.11	14.33		1582
			(31.40)	(3.95)	(13.77)		

[a] Calculated value in parenthesis.

1-Allyl-3,5-dimethylpyrazole silver(I) nitrate: $AgNO_3(ADMP)$

A mixture of silver nitrate (0.01 mol) and ADMP (0.01 mol) in chloroform (30 ml) was boiled under reflux with stirring and undissolved silver nitrate was removed by filtration. The faintly brown oil remaining after removal of solvent by distillation in vaduo was redissolved in ethanol. An adequate amount of n-hexane was added and after the solution refrigerated for a few days, colourless crystals were obtained (yield *ca.* 20%). Analytical data is given in Table I.

Measurements

Infrared spectra (400–4000 cm^{-1}) were recorded on a Hitachi EPI-G2 spectrophotometer using KBr discs except for $AgNO_3$(ADMP), whose spectrum was recorded as nujol mull because of its low thermal stability. Samples in solution were measured using a NaCl cell (0.025 mm). UV and visible spectra (210 to 700 nm) were recorded on a Hitachi EPS-3 using methanol and ethanol as a solvent. Cuprous complexes were examined under a nitrogen atmosphere. ^1H NMR spectra were recorded on a JEOL-PS100 instrument at 100 MHz. TMS and chloroform were used as an internal standards.

Results and Discussion

Whether an olefin is coordinated to a metal or not, is conveniently judged by infrared spectroscopy. The vibrational frequency of the C=C double bond is usually lowered as the result of the coordination to a metal.

Free ADMP has a band at 1646 cm^{-1} which is assigned to the C=C vibration of the allyl group. All $M(II)X_2(ADMP)_2$ complexes absorb in the same region as free ADMP (Table I), which suggests that the olefinic part of the ligand is free and that the ligand probably coordinates to the metal solely through the pyrazolyl nitrogen in a simple N-donor fashion. Tetrahedral coordination around Co(II) is suggested by the visible spectrum (Table III), which corresponds well with that of CoX_2(1,3,5,-trimethylpyrazole)$_2$[5].

On the other hand, Cu(I) and Ag(I) complexes show no absorption in the range 1600–1700 cm^{-1}. The silver complex, $AgNO_3$(ADMP), exhibits a new band at 1582 cm^{-1}, which may be assigned to a shifted C=C vibration. In Cu(I) complexes, however, assignment is difficult because of overlap with the strong ring C=C or C=N vibration at *ca.* 1550 cm^{-1}. Since no other additional absorption is observed in the 1500 to 1700 region, the shoulder at *ca.* 1540 cm^{-1} is assigned to the shifted C=C band. The allyl group double bond is undoubtedly coordinated to the metal in these M(I) complexes. The lowered shifts, $\Delta\nu$ (C=C), are 64 cm^{-1} for $AgNO_3$(ADMP) and *ca.* 100 cm^{-1} for CuX(ADMP).

For 2-allylpyridine, Yingst found shifts, $\Delta\nu$ (C=C), of 87 cm^{-1} for CuCl and 58 cm^{-1} for the $AgNO_3$ complex[2]. As to phosphine– and arsine–olefin ligand types, Bennett prepared and characterized Ag(I) and Cu(I) complexes of (*o*-allylphenyl)diphenylphosphine (app), (*o*-methallylphenyl)diphenylphosphine (mpp) and (*o*-allylphenyl)dimethylarsine (ama)[6]. Experimentally, he found that $(CuX\cdot app)_2$ (X = Cl, Br, I), $(CuI\cdot mpp)_2$ and $AgNO_3$(ama) contained a metal–olefin bond, with $\Delta\nu$(C=C) 78 cm^{-1} for $(CuBr\cdot app)_2$ and 50 cm^{-1} for $AgNO_3$(ama). In cyclooctadiene and norbornadiene CuCl complexes, *ca.* 100 cm^{-1} shifts were observed[7].

In Cu(I)–ADMP or Ag(I) complexes, relatively larger shifts $\Delta\nu$(C=C) compared with those of other Y–olefin (Y = N, P, As) chelates and comparable to those of the simple olefin complexes of Cu(I) are observed.

In addition to the above infrared evidence, coordination of the olefinic moiety is also supported by our preliminary X-ray analysis[8].

In spite of these factors supporting olefin-coordination to Cu(I) or Ag(I), definite evidence is not obtained in ^1H NMR spectra of the Cu(I)–ADMP and Ag(I)–ADMP complexes. In every case, all signals

TABLE II. ^1H NMR Data of the Complexes.

Compound	Solvent	Chemical Shift (ppm, δ value)							Coupling Constants (Hz)			
		(a)*	(b)	(c)	(d)	(e)	(f)	(g)	$\lvert J_{de}\rvert$	$\lvert J_{ef}\rvert$	$\lvert J_{eg}\rvert$	$\lvert J_{fg}\rvert$
free ADMP	$CDCl_3$	2.06	5.65	2.09	4.46	5.80	4.82	5.01	6	17	10	2
$ZnCl_2(ADMP)_2$	$CDCl_3$	2.21	5.94	2.26	5.19	5.89	4.92	5.17	6	17	10	1.5
CuCl(ADMP)	$CHCl_3$	2.28	6.0**	2.34	4.69	5.84	5.08	5.30	5	17	10	0
	CH_3CN	2.17	5.92	2.20	4.70	5.85	4.92	5.13	6	17	10	2
CuBr(ADMP)	$CHCl_3$	2.24	6.0**	2.36	4.69	5.87	5.12	5.31	5	16	10	0
CuI(ADMP)	CH_3CN	2.15	5.87	2.20	4.65	5.91	4.99	5.16	5	18	10	1
$AgNO_3$(ADMP)	$CDCl_3$	2.24	5.93	2.27	4.74	5.93	5.08	5.26	6	16	10	2
CuBr(ADMPBr)	CH_3CN	2.20	–	2.23	4.71	5.95	5.02	5.21	6	16	10	1.5

* Notations as in I. ** Broad signal.

TABLE III. Visible Spectra of Co(II) Complexes.

Complex	Band Maxima (kK)	Solvent
$CoCl_2(ADMP)_2$	17.2 sh(85),[a] 16.0 sh(130), 15.2(145)	EtOH
$CoBr_2(ADMP)_2$	16.9 sh(70), 15.6 sh(100), 14.9(110)	EtOH
$CoCl_2(tmPz)_2$[b c]	17.1 sh(160), 15.1(270)	EtOH
$CoBr_2(tmPz)_2$[b c]	16.5(71), 15.3 sh(111), 14.9(124)	EtOH

[a] Molar extinction coefficient, ε, in parenthesis. [b] Ref. 5. [c] tmPz = 1,3,5-trimethylpyrazole.

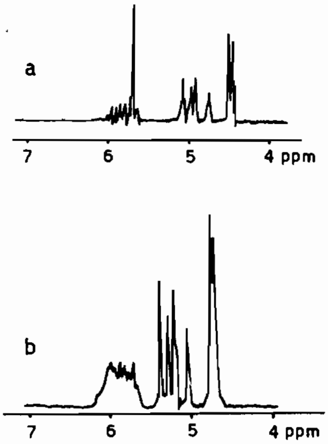


Figure 1. ^1H NMR spectra of ADMP (a) and CuCl(ADMP) (b) (δ = 4–7 ppm).

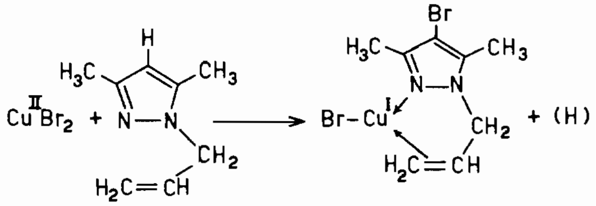
are shifted 0.2–0.3 ppm to lower magnetic field. Neither the chemical shifts of the olefinic protons of the allyl group nor the spin coupling constants between them show any distinctive change from those of free ADMP and of the Zn(II) complex in which the olefinic moiety is free (Table II).

In most of the metal–olefin complexes, the ^1H NMR of the olefinic protons are significantly shifted upfield and the associated decreases in spin coupling constants are observed[9]. In Cu(I) and Ag(I), however, downfield shifts of the olefinic protons upon coordination are frequently observed[10–12]. These downfield shifts or the deshielding effects accompanying complex formation is regarded as being due to the predominant σ-component of the metal–olefin bond[11].

Similarly unchanged ^1H NMR were noted by Bennett for Cu(I) and Ag(I) complexes containing app, mpp and ama ligands[6]. In our case, the spectra can be interpreted on the basis of dissociation of the metal–olefin bond in solution before considering the bond character, because the ir spectrum of CuCl(ADMP) in chloroform solution shows the C=C vibration band at 1643 cm^{-1} and the shoulder assigned to the shifted ν(C=C) in the solid state is lost. Such lability of Cu(I) and Ag(I)–olefin bonds are generally known[12, 13].

Another characteristic of the ^1H NMR is a remarkable broadening of the 4-position H(b) signal in the ring, which is peculiar to CuCl and CuBr complexes (Figure 1). The proton H(b) chemical shifts in these cases could not be exactly determined owing to overlap with the methyne proton of the allyl group. Since the broad signal is sharpened when the solvent is changed from chloroform to acetonitrile, it must be due to $CHCl_3$ solvent interaction, *e.g.* to hydrogen bonding or to proton exchange. No such broadening is observed in Ag(I) or Zn(II) complexes.

In any case, the broadening indicates some activation of the 4-position H(b) of the ring in the presence of Cu(I) and must be closely related to the specific reaction of ADMP with $Cu(II)Br_2$:



Cupric(II) bromide reacted with ADMP in ethanol, though the isolated crystals proved to be the cuprous(I) compound, CuBr(ADMPBr), as opposed to the cupric complex $CuBr_2(ADMP)_2$. The same product was obtained when the reaction was carried out under nitrogen or in acetonitrile solution. The reaction characteristics are as follows: (i) The reaction is peculiar to $CuBr_2$, which is a well-known reducting reagent. With $CoBr_2$, $ZnBr_2$ or $CuCl_2$, such a reaction docs not occur. (ii) The allyl group is indispensable for the reaction, *e.g.*, 1-phenyl-3,5-dimethylpyrazole (PhDMP) and $CuBr_2$ gives $CuBr_2(PhDMP)_2$. (iii) With ATMP, the 4-position of which is occupied by a methyl group, cupric bromide cannot be reduced.

It is well known that pyrazole and its derivatives readily undergo nucleophilic substitution[14] at the 4-position. Therefore it is by no means surprising that such substitution may be prompted by suitable reactive reagents. More interesting is the fact that the reaction is induced by the relatively higher stability of Cu(I) than Cu(II) in metal–olefin bond formation.

The hydrogen atom liberated from the pyrazole ring seems to be trapped somewhere in the system, for no generation of gas can be detected.

The ir spectrum of CuBr(ADMPBr) exhibits no absorption due to free olefin. The ^1H NMR of the complex is scarcely different from that of the free ligand as is the case for ADMP complexes. On the basis of these spectroscopic characteristics we propose a structure for CuBr(ADMPBr) shown in IIa.

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