Mononuclear and Polynuclear Copper Complexes of Some Substituted Hydrazones

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The reactivity of a series of potentially tetraden-tate hydrazone ligands, involving pyridyl and imid-azolyl substituent groups, towards copper(II) salts has been examined. Both mononuclear and polynuclear derivatives are obtained with some ligands and in some cases redox reactions are observed in which, when water is a significant solvent component, nitro-gen gas evolution indicates the formation of copper(I) derivatives. The reduction is assumed to occur by initial hydrolysis of the hydrazone ligand, forming hydrazine as one product, which reduces copper(II) to copper(I). However the copper(I) ions bind prefer-entially to unoxidized ligand thus limiting the extent to which reduction occurs. In the presence of electro-negative ligands the copper(II) complexes are stabil-ized in some cases, while in one case a mixed valence polynuclear species is produced. Preliminary details of the X-ray structure of [Cu(IMAA)Br₂]·H₂O (IM-AA = (1-methyl-2-imidazolyl)aldazine) indicate a mononuclear, five-coordinate, system involving un-symmetrical tridentate ligand, a structural feature which is apparent in most other mononuclear species.

Introduction

Substituted diazine ligands (*e.g.* phthalazines [1–13], pyridazines [1, 2, 7, 14, 15], and hydrazines [16–21]) are capable of binding two metal ions in close proximity and in many cases [1, 4, 5, 7, 13], antiferromagnetic exchange occurs between the two metal centres via the bridging ligands. Pyridine-2-aldehydeazine (PAA), derived from the condensation of pyridine-2-aldehyde and hydrazine, has been shown to produce metal complexes with a variety of different stereochemistries [16–18]. This arises largely as a result of free rotation about the N–N bond, such that four isomeric forms of the ligand are possible as shown in Fig. 1.

Stratton and Busch [18, 19] reported the systems [M₂(L)₃]⁴⁺ (where M = Fe(II), Co(II), Ni(II); L = PMK, PAA (Fig. 1)) where the ligand was predicted to adopt conformation 1b (Fig. 1) as shown in Fig. 2.
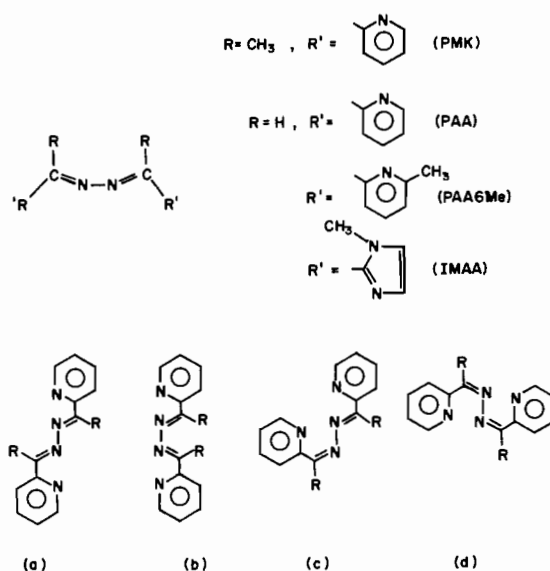
Fig. 1. The four isomeric forms of the ligand.
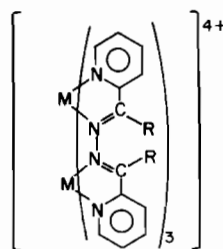
Fig. 2. Structural representation for [M₂(L)₃]⁴⁺ (M = Fe(II), Co(II), Ni(II); L = PMK, PAA) [18, 19].

Experiments with models indicated this to be sterical-ly feasible provided each ligand is twisted by 60° about its N–N bond. Similar copper complexes have not been observed. However a recent report [21] on the X-ray crystal structures of a mono- and binuclear copper(II) complex of 2-pyridylmethylketazine (PMK) has confirmed some of the earlier predictions made by Stratton and Busch concerning the triden-tate and tetradentate coordination of PMK and PAA.

Our interest in substituted hydrazine ligands rests with their potential for forming binuclear copper(II)

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complexes as models for the active sites of the type III containing copper proteins and oxyhemocyanin. Magnetic studies have shown that strong antiferromagnetic exchange exists between the two copper(II) centres in *Megathura crenulata* oxyhemocyanin $(-2J \geqslant 1250$ cm$^{-1})$ [22, 23] and *Rhus vernicifera* laccase $(-2J \geqslant 1000$ cm$^{-1})$ [23]. Metal-metal separations in oxyhemocyanins are reported to be in excess of 3.50 Å [24] and 3.67 Å [25] according to EXAFS studies. In our previous studies [13] on antiferromagnetically coupled binuclear copper(II) complexes of substituted phthalazine ligands, which have hydroxide bridges, we have shown that the dimensions of the binuclear centres can be tuned by varying a third bridging group such that the exchange increases with increasing oxygen bridge angle. A linear correlation between the exchange integral and Cu–O–Cu angles has been established [26]. However, because of the rigid phthalazine ring with two nitrogens fixed in adjacent positions, a limitation may have been imposed upon the degree of expansion of the Cu–O–Cu angle. The more flexible hydrazine ligands were thus considered in terms of their potential to generate systems with more expanded binuclear centres.

In this study we have examined the copper coordination chemistry of two related ligands (2-pyridyl-4-methyl)aldazine (PAA6Me) and (1-methyl-2-imidazolyl)aldazine (IMAA) (Fig. 1) (previously unreported) and also report some additional studies on PAA and PMK. The ligand IMAA has been shown to form predominantly monomeric species involving tridentate ligand and this is confirmed by an X-ray study on the complex [Cu(IMAA)(Br)$_2$]·H$_2$O. With PAA6Me, in a rather unusual type of reaction, copper(I) complexes are produced, in most cases, by apparent metal ion mediated ligand hydrolysis producing hydrazine, which acts as a reducing agent. Reduction reactions are observed, but to a lesser extent, with PMK and IMAA and the presence of water is indicated to be a controlling factor in this sort of reaction. Limiting the water content of reaction solvents by the use of triethylorthoformate (TEOF) as a solvent component leads to the formation of copper(II) complexes even in the most sensitive cases.

Experimental

Electronic spectra were recorded with a Cary 17 spectrometer and infrared spectra with a Perkin-Elmer Model 283 spectrometer. Magnetic susceptibilities were obtained at room temperature by the Faraday method using a Cahn Model #7600 Faraday Magnetic Susceptibility system, coupled to a Cahn gram electrobalance. Nuclear magnetic resonance spectra were run as solutions in deuterochloroform using a Bruker WP80 spectrometer and mass spectra

were run using a V.G. Micromass 7070 HS with the direct insertion probe. Microanalyses were carried out by Canadian Microanalytical Service, Vancouver (C, H, N). Metal analyses were determined by atomic absorption with a Varian Techtron AA-5, after digestion of the samples in concentrated HNO$_3$ or *aqua regia*.

Ligands

PAA [16], PMK [19] and PAA6Me [27] were prepared according to literature procedures.

(1-methyl-2-imidazolyl)aldazine (IMAA)

Anhydrous hydrazine was reacted with N-methylimidazole-2-carboxyaldehyde [28] in a ratio of 2:1 in absolute ethanol. The solution mixture was refluxed for 24 h. It was observed that yellow crystals precipitated from solution after 4 h of reflux. The yellow crystalline material was recrystallized from ethanol (mp 257–260 °C). *Anal.* calcd. for C$_{10}$H$_{12}$-N$_6$: C 55.5, H 5.55, N 38.9; found: C 55.3, H 5.49, N 39.1. Mass spectrum, major mass peaks (m/e (relative intensity)) 216(42) P, 173(94), 158(28), 134(74), 108(72), 82(88). ^{1}H nmr (CDCl$_3$) (δ (relative intensity)) 4.05(30) (singlet, methyl), 6.98(10) (singlet imidazole H$_4$), 7.17(10) (doublet, imidazole H$_5$) 8.60(10) (singlet azomethine CH). In the mull infrared red spectrum, a strong sharp absorption at 1636 cm^{-1} is observed associated with CN stretch.

Copper Complexes

[Cu(IMAA)(NO$_3$)$_2$]·H$_2$O (VI)

IMAA (1.00 g; 4.63 mmol) dissolved in 100 ml of methanol was added to a solution of Cu(NO$_3$)$_2$·3H$_2$O (2.80 g; 11.57 mmol) dissolved in 50 ml of methanol at room temperature. The solution turned dark green upon mixing. After a few minutes a green precipitate formed which was filtered off, washed thoroughly with methanol and ether and dried *in vacuo* at 70 °C for several hours. Other complexes, (I, II, VII, IX, XI, XIV) were prepared similarly using an excess of copper salt and the appropriate ligand. Complex X was prepared similarly by reacting an aqueous solution of cupric chloride with a methanol solution of ligand. A small amount of gas (nitrogen) was evolved during this reaction. Complex VIII was obtained as crystals of X-ray quality by using a solvent mixture of DMF/H$_2$O and a similar procedure.

[Cu$_2$(PMK)$_2$(OH)](ClO$_4$)$_3$·MeOH (IV)

PMK (0.2 g; 0.84 mmol) was dissolved in methanol containing ten percent triethylorthoformate (TEOF) (50 ml) and added to a refluxing solution of Cu(ClO$_4$)$_2$·6H$_2$O (0.64 g; 0.17 mmol) in the same solvent mixture (50 ml). A pale green precipitate formed after 30 min, which was filtered, washed with 10% TEOF/methanol and dried *in vacuo* at 70 °C for 2 h.

Complexes **XII** and **XIII** were prepared in a similar manner in the same reaction mixture.

[Cu₂(PMK)Br₄] (V)

PMK (0.5 g; 2.1 mmol) was added to a solution of $CuBr_2$ (1.4 g; 6.30 mmol) dissolved in water (100 ml). The mixture was heated to reflux for 45 mins. Initially the ligand dissolved and after a few minutes a green precipitate formed during reflux. The mixture was left to cool at room temperature and the product was filtered off, washed thoroughly with ether and dried *in vacuo* at 70 °C for several hours. Complexes **III** and **XII** were prepared similarly using an excess of copper salt and the appropriate ligand. For both complexes gas evolution was observed during reflux. Routine tests showed that the gas was nitrogen.

Satisfactory analytical data have been obtained for these complexes and are reported in Table I.

Results and Discussion

Stratton and Busch [16—19] have relied on the C—N stretching region in the infrared to determine whether the ligands PAA and PMK are tridentate or tetradentate, forming mononuclear complexes with five-membered and six-membered chelate rings or binuclear complexes with only five membered chelate rings. The tridentate chelation of the ligands is accompanied by a distinct splitting of the pyridine ring breathing vibration and of the C—N stretching mode of the azine link, whereas tetradentate chelation should give rise to only single bands in these two regions. In our studies on some copper complexes of PMK and PAA, which are previously unreported, we have used these infrared observations (Table II) in assessing the structural features of complexes **I—V**. For complex **III** the pyridine ring breathing vibration was not observed and appeared to be overlapped with the very broad absorption of the perchlorate group in the region 1000—1100 cm⁻¹. Complex **V** was found to exhibit no splitting in the C—N stretching region or of the pyridine ring vibration indicative of a symmetrically coordinated ligand. Complexes **I** and **II** have normal magnetic moments (Table III) consistent with monomeric entities and d—d absorption (Table III) consistent with five-coordinate copper centres. Infrared bands at 1749 cm⁻¹ and 1725 cm⁻¹ for complex **I** are indicative of a $(\nu_1 + \nu_4)$ nitrate combination associated with monodentate nitrate groups [29] and conductance data [30] in nitromethane ($\Lambda_M = 46.0$ mho mol⁻¹ cm²) indicate an essentially neutral species which has undergone partial solvolysis. The solid state structure of **I**, therefore, appears to be similar to that of $Cu(PMK)(NO_3)_2$ [21] and involves a tridentate ligand, bound at both pyridine nitrogens and one azine nitrogen, with two coordinated monodentate nitrate groups in a five-coordinate structure. Similarly with complex **II**, the ligand acts in a tridentate fashion with the remaining two positions occupied by two water molecules and the perchlorates existing as ionic species (I.R. data show a very broad band of 1080 cm⁻¹ associated with ionic perchlorate groups).

On examination of the infrared data for complex **III** tridentate chelation of the ligand is apparent. **III** has an intense visible band at 21 500 cm⁻¹, which appears not to be d—d in origin and may be associated with a charge transfer transition. The absence of any d—d absorption suggests that the copper ion is in the 1+ oxidation state which is substantiated further by the very low room temperature magnetic

TABLE I. Analytical and Other Data.

Compound		Colour	Found (%)				Calcd (%)			
			C	H	N	M	C	H	N	M
I	[Cu(PAA)(NO₃)₂]·0.25H₂O	green	28.65	2.12	11.18	15.91	28.32	2.75	11.01	15.80
II	[Cu(PAA)(H₂O)₂](ClO₄)₂	brown	35.82	2.15	20.58	13.06	35.82	2.61	20.89	12.48
III	[Cu(PMK)(H₂O)](ClO₄)	brown	39.85	3.43	13.51	15.21	40.28	3.84	13.43	15.23
IV	[Cu₂(PMK)₂(OH)](ClO₄)₃·MeOH	light green	37.28	3.41	12.08		36.61	3.47	11.78	
V	[Cu₂(PMK)Br₄]	dark brown	24.57	2.04	8.17	18.54	24.52	1.72	8.11	17.52
VI	[Cu(IMAA)(NO₃)₂]·H₂O	green	28.47	3.24	26.47	15.39	28.47	3.32	26.57	15.00
VII	[Cu(IMAA)(H₂O)₂](ClO₄)₂·0.5H₂O	khaki	22.82	2.82	15.97	13.25	22.92	3.24	16.05	13.27
VIII	[Cu(IMAA)Br₂]·H₂O	brown	26.08	2.35	18.03		26.14	3.48	18.30	
IX	[Cu₃(IMAA)₂Cl₆]·H₂O[a]	green	28.19	2.93	19.57	22.29	28.12	3.05	19.68	22.31
X	[Cu₃(IMAA)₂Cl₅][b]	dark green	30.06	2.73	20.79	23.62	30.06	3.26	21.04	23.88
XI	[Cu(PAA6Me)(H₂O)](ClO₄)·0.5MeOH	red brown	39.81	3.31	12.92	14.97	40.10	3.92	12.90	14.63
XII	[Cu₂(PAA6Me)Br₂]	brown	32.31	2.46	10.64	24.27	32.00	2.67	10.67	24.19
XIII	[Cu(PAA6Me)Br₂]·MeOH	green	36.00	3.09	11.11		36.50	3.64	11.34	
XIV	[Cu₂(PAA6Me)Cl₄]	brown	32.83	2.97	10.92	25.29	33.10	2.76	11.00	25.01

[a]Found Cl 23.84%; calcd. Cl 24.95%.   [b]Found Cl 22.37%; calcd. Cl 22.15%.

TABLE II. Infrared Data (cm^{-1}).

	Compound	ν CN	Other
I	[Cu(PAA)(NO$_3$)$_2$]·0.25H$_2$O	1631, 1583	3400 (H$_2$O), 1749, 1725 ($\nu_1 + \nu_4$, NO$_3^-$) 1022, 1010 (pyr)
II	[Cu(PAA)(H$_2$O)$_2$](ClO$_4$)$_2$	1631, 1585	3500 (H$_2$O), 1080 (ClO$_4^-$), 1025, 1010 (pyr)
III	[Cu(PMK)(H$_2$O)](ClO$_4$)	1678, 1588	3490 (H$_2$O), 1080 (ClO$_4^-$)
IV	[Cu$_2$(PMK)$_2$(OH)](ClO$_4$)$_3$·MeOH	1600, 1576	3560 (OH), 3500sh (MeOH), 1100 (ClO$_4^-$), 1025, 1018 (pyr)
V	[Cu$_2$(PMK)Br$_4$]	1590	1020 (pyr), 255 (Cu–Br)
VI	[Cu(IMAA)(NO$_3$)$_2$]·H$_2$O	1615, 1579	3400 (H$_2$O), 1766, 1756, 1714 ($\nu_1 + \nu_4$, NO$_3^-$)
VII	[Cu(IMAA)(H$_2$O)$_2$](ClO$_4$)$_2$·0.5H$_2$O	1612, 1573	1097, 1075 (ClO$_4^-$)
VIII	[Cu(IMAA)Br$_2$]·H$_2$O	1612, 1571	3460 (H$_2$O), 258, 234 (Cu–Br)
IX	[Cu$_3$(IMAA)$_2$Cl$_6$]·H$_2$O	1618, 1575	3460 (H$_2$O), 300, 290, 280 (Cu–Cl)
X	[Cu$_3$(IMAA)$_2$Cl$_5$]	1615, 1577	300, 280 (Cu–Cl)
XI	[Cu(PAA6Me)(H$_2$O)](ClO$_4$)·0.5MeOH	1623, 1584	3510 (MeOH, H$_2$O), 1108, 1089 (ClO$_4^-$)
XII	[Cu$_2$(PAA6Me)Br$_2$]	1618, 1582	305 (Cu–N) 236 (Cu–Br)
XIII	[Cu(PAA6Me)Br$_2$]·MeOH	1630, 1605, 1590, 1580	320 (Cu–N)
XIV	[Cu$_2$(PAA6Me)Cl$_4$]	1633, 1588	290, 278 (Cu–Cl)

TABLE III. Electronic Spectra (Mull Transmittance) (cm^{-1}) and Magnetic Moments.

	Compound	d--d	CT	μ(BM)Cu (room temperature)
I	[Cu(PAA)(NO$_3$)$_2$]·0.25H$_2$O	[10800]14900	[20000]29400	1.87
II	[Cu(PAA)(H$_2$O)$_2$](ClO$_4$)$_2$	[14900]	20800	1.80
III	[Cu(PMK)(H$_2$O)](ClO$_4$)		21500, 28600	0.30
IV	[Cu$_2$(PMK)$_2$(OH)](ClO$_4$)$_3$·MeOH	10000, 13800	26000	1.80
V	[Cu$_2$(PMK)Br$_4$]	13900	18900	1.76
VI	[Cu(IMAA)(NO$_3$)$_2$]·H$_2$O	16400	23800	1.79
VII	[Cu(IMAA)(H$_2$O)$_2$](ClO$_4$)$_2$·0.5H$_2$O	16100	26300	2.01
VIII	[Cu(IMAA)Br$_2$]·H$_2$O	14500	23300	1.73
IX	[Cu$_3$(IMAA)$_2$Cl$_6$]·H$_2$O	15400 15000(183)[a]	25000 26000(17500)[a]	1.81
X	[Cu$_3$(IMAA)$_2$Cl$_5$]	15000	24100	1.55
XI	[Cu(PAA6Me)(H$_2$O)](ClO$_4$)·0.5MeOH		20000, 28600	0.48
XII	[Cu$_2$(PAA6Me)Br$_2$]		[20800]	0.45
XIII	[Cu(PAA6Me)Br$_2$]·MeOH	8900, 13800	27400	1.90
XIV	[Cu$_2$(PAA6Me)Cl$_4$]	[11800]13600	20000, 27000	1.66

[a]Solution spectrum in methanol (molar extinction coefficient) [ ] = shoulder.

moment. The residual paramagnetism is probably caused by partial oxidation on exposure to air. Infrared spectra show that the perchlorate group exists as an ionic species and that water is present. The complex is therefore proposed to be a four-coordinate mononuclear copper(I) complex with a tridentate ligand and a coordinated water molecule occupying the fourth position. This reaction of the ligand with a Cu(II) salt in an aqueous solvent, resulting in a redox reaction with the formation of a Cu(I) complex and nitrogen evolution is also observed in other cases and will be discussed later.

If water is eliminated during the reaction of copper perchlorate with PMK a pale green complex (IV) is obtained which is clearly a copper(II) deriva-tive. Infrared data suggest that the ligand is tridentate and that a hydroxide bridge exists between the two copper(II) centres in the proposed binuclear structure. The perchlorate groups are ionic in nature as indicated by infrared data and conductance measurements in nitromethane ($\Lambda_M = 253$ mho mol^{-1} cm^{-2}) indicate a 1:3 electrolyte. The low energy d–d absorption is consistent with a distorted four-coordinate stereochemistry at copper and the normal magnetic moment, indicative of a system without antiferromagnetic exchange, implies a rather small bridge angle at oxygen [26].

Infrared data indicate complex **V** to have a symmetrical tetradentate ligand and absorption at 255 cm^{-1} indicates the presence of terminal copper–

bromine bonds. A near normal room temperature magnetic moment suggests either an uncoupled system or one involving weak spin exchange and d—d absorption at $13\,900$ cm^{-1} is consistent with a distorted four-coordinate species. It is reasonable to assume therefore that this compound is structurally similar to $Cu_2(PMK)(Cl)_4$, which has a binuclear structure with the conformation of the ligand as shown in Fig. 1(a) [21]. It is noted that for Cu_2-$(PMK)(Cl)_4$ an exchange integral $-2J = 52$ cm^{-1} exists, which is assumed to occur solely via the bridging N—N linkage [21]. A structural representation of V is shown in Fig. 3.

The ligand IMAA forms predominantly mononuclear derivatives in which the ligand appears to coordinate in a tridentate fashion. Preliminary details of the X-ray structure of VIII (Fig. 4) [31] show that the ligand utilizes two imidazole nitrogen atoms (N_1, N_4) and one diazine nitrogen (N_3) in coordination, thus forming a five-membered and a six-membered ring. The other two coordination positions around the distorted square pyramidal copper centre are occupied by bromine atoms. Relevant bond distances and angles around the copper centre are given in Table IV. This structure is analogous to that reported by O'Connor [21] for the complex [Cu-$(PMK)(NO_3)_2$], in which the conformation of the ligand is essential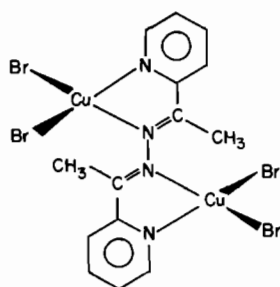ly the same, but the stereochemistry at copper is closer to a trigonal-bipyramid. The major difference between these two systems involves the azomethine carbon centres; a methyl group is bound to each carbon atom in PMK whereas in IMAA protons exist at these centres. The presence of the methyl groups in PMK may, in part, be responsible for the difference in stereochemistry between these two systems.
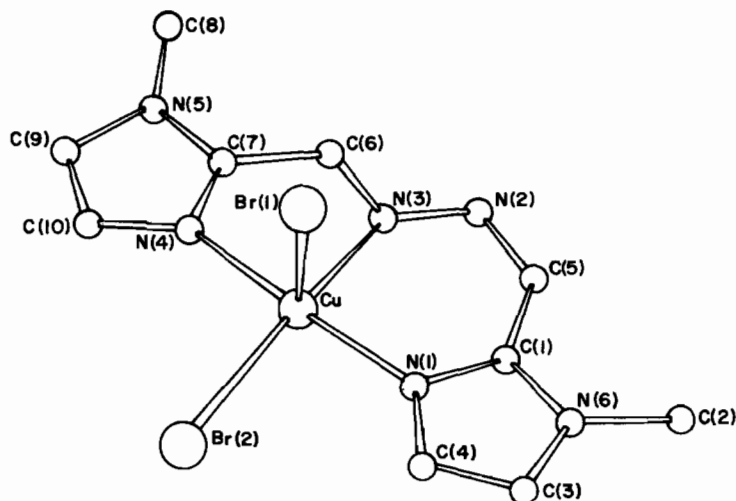
[Cu(IMAA)Br$_2$]·H$_2$O has a near normal magnetic moment, consistent with a monomeric entity, and d—d absorption consistent with a five-coordinated derivative. Infra red bands at 234 and 258 cm^{-1} are associated with the *cis*-arrangement of copper—bromine bonds. The similarity of the infrared spectra of compounds VI and VII with that of VIII, especially in the area of CN stretch, suggests that in both cases tridentate ligands are involved, in which the mode of coordination is the same as that in VIII. A shift to higher energy of the d—d absorption is consistent with the coordination of stronger ligands at the copper centres in VI and VII. In VII the perchlorate groups appear to be ionic and so the remaining coordination sites are assumed to be occupied by water molecules. For VI there are no infrared bands indicative of coordinated water and $(\nu_1 + \nu_4)$ combination bands associated with the nitrate groups suggest one bidentate nitrate and ionic nitrate group [29]. Conductance measurements in nitromethane [30] suggest a 1:1 electrolyte ($\Lambda_M = 76.0$ mho mol^{-1} cm^2). Five coordinate structures similar to VIII are therefore suggested for VI and VII.

Unlike the binuclear copper chloride complex of PMK, $Cu_2(PMK)Cl_4$ [21], compound IX, which was prepared in methanol, appears to be a polynuclear derivative involving three metal centres per two ligands. Elemental analysis for this system leaves no doubt as to the empirical formula. Trinuclear copper-(II) complexes have been observed [11] with other

Fig. 3. Proposed structure for [Cu$_2$(PMK)Br$_4$] (V).

Fig. 4. Preliminary X-ray structure for [Cu(IMAA)Br$_2$]·H$_2$O (VIII) ($R = 0.04$).

TABLE IV. Selected Bond Lengths and Bond Angles for $[Cu(IMAA)Br_2]H_2O$ ($R = 0.04$).

Bond	Length (Å)	Bonds	Angle (deg.)
Cu–Br(1)	2.610(2)	Br(1)–Cu–Br(2)	107.2(1)
Cu–Br(2)	2.434(2)	Br(1)–Cu–N(3)	101.0(3)
Cu–N(3)	2.08(1)	Br(1)–Cu–N(4)	97.6(3)
Cu–N(4)	1.99(1)	Br(1)–Cu–N(1)	95.4(3)
Cu–N(1)	1.97(1)	Br(2)–Cu–N(3)	151.4(3)
		Br(2)–Cu–N(4)	91.8(3)
		Br(2)–Cu–N(1)	93.9(3)
		N(3)–Cu–N(4)	80.2(4)
		N(3)–Cu–N(1)	87.6(4)
		N(4)–Cu–N(1)	163.6(4)

potentially binucleating diazine ligands (*e.g.* 1,4-di-(2'-pyridyl)aminophthalazine), in which the proposed structure involved tetradentate ligands binding a linear arrangement of hydroxy bridged copper(II) centres. A comparison of the CN stretching region of the infrared spectrum of IX with those of the other three IMAA complexes suggests that the ligand is probably tridentate in IX also. Other infrared bands at 280, 290 and 300 cm^{-1} are associated with terminal copper chlorine bonds. The normal magnetic moment for this system suggests the absence of antiferromagnetic exchange in the polynuclear structure and the lack of visible absorption associated with such species as $CuCl_4^{2-}$, $Cu_2Cl_6^{2-}$ [32] rules out the possibility of IX as an ionic system involving either a mononuclear or binuclear cation.

Reaction of cupric chloride and IMAA in aqueous methanol led to a green crystalline product (X), which formed slowly (unlike IX which precipitated immediately on mixing the methanolic solutions of ligand and metal salt). Again analysis, involving five elements, confidently assigns the empirical formula $[Cu_3(IMAA)_2Cl_5]$. A general spectral similarity between IX and X invites the suggestion that the two compounds are structurally similar, but the presence of only five chlorine atoms in X indicates the possibility of a system with a mixed oxidation state involving two copper(II) centres and one copper(I) centre. There are numerous structural possibilities for IX and X, based on a trinuclear cluster of copper centres, and speculation, based on the data available, is difficult. An X-ray structural investigation of X will be attempted to resolve this situation.

Of all the ligands studied PAA6Me formed copper-(I) complexes most readily. Spontaneous reduction was observed in the formation of XI and XII, and in the reaction between copper(II) nitrate and PAA6Me in methanol, but the complex formed in this case could not be obtained in an analytically pure state and so is not reported. The copper(II) complex $[Cu_2(PAA6Me)Cl_4]$ (XIV) appears to be a binuclear derivative. Infrared and electronic spectral data are consistent with somewhat tetrahedrally distorted four-coordinate CuN_2Cl_2 centres and it is reasonable to assume that this compound is structurally similar to $[Cu_2(PMK)Cl_4]$ (*cf.* Fig. 3). The slightly reduced magnetic moment observed for XIV, probably indicative of relatively weak intradimer exchange, is consistent with the behaviour of $[Cu_2(PMK)Cl_4]$ [21]. The presence of two CN bands in the infrared spectrum of XIV would, using earlier criteria [16–19], suggest the presence of unsymmetrical tridentate ligand. However, other considerations favour the presence of symmetrical, tetradentate ligand, thus casting doubt on the general applicability of such criteria.

Compound XI is a copper(I) derivative and is likely to be structurally similar to III, involving a tridentate ligand and a four-coordinate copper(II) centre. However the possibility of a polymeric derivative, involving tetradentate ligand, should not be ruled out in this case. The non-zero magnetic moment appears to be the result of the presence of a small amount of a copper(II) species which could result from partial oxidation of the complex on exposure to air. In general this sytem appeared to be relatively stable on exposure to air for short periods of time.

Compound XII is a binuclear system involving copper(I) centres, and is produced by reaction of copper(II) bromide and PAA6Me in water. The weak paramagnetism associated with this compound is again considered to be due to partial oxidation of the complex on exposure to air. An infrared absorption at 236 cm^{-1} suggests the presence of terminal copper-bromine bonds and a reasonable structure for the system would involve tetradentate ligand, with conformation 1(a) (Fig. 1), and two three-coordinate copper(I) centres. This would differ considerably from the structure proposed by Stratton and Busch [18] for the complex $[Cu_2(PAA)Br_2]$, in which four halogen bridged copper(I) centres are sandwiched between two adjacent tetradentate ligands.

Reaction of copper(II) perchlorate with PAA6Me in TEOF/methanol produced just the copper(I) complex, XI, whereas with copper bromide, under similar conditions, two compounds resulted. Initially XII was

obtained as a brown insoluble solid, followed by a green crystalline product, **XIII**, from the mother liquor. This compound is clearly a mononuclear copper(II) derivative with a normal magnetic moment and the rather low energy d—d absorption suggests a somewhat tetrahedrally distorted four-coordinate system. The appearance of four infrared bands in the CN stretching region is unusual and suggests the possible presence of four different CN sites in the coordinated ligand which would be consistent with bidentate coordination of PAA6Me.

Many of the complexes described exhibit intense absorptions in their electronic spectrum around 20000 cm^{-1}. These are clearly not d—d in nature and are associated with charge transfer, although, at this stage their origin remains in question.

Previous studies on the ligands PAA [18] and PMK [21] make no reference to possible reduction reactions involving copper(II), even in aqueous solvents, although the range of metal salts studied was somewhat limited. Reaction of PAA with cupric chloride in water and ethanol produced copper(II) derivatives as was the case in reactions involving cupric chloride and nitrate with PMK in alcohols. As part of this study we investigated the reaction of PAA with cupric nitrate and perchlorate in methanol and in both cases copper(II) derivatives resulted with no evidence for a redox reaction. However with PMK and copper(II) perchlorate, in water, nitrogen gas evolution signalled the formation of a copper(I) species, while a similar reaction involving copper bromide produced a copper(II) derivative. With IMAA the only case where reduction took place was in the formation of **IX**, a partially reduced system, from aqueous methanol. In the case of the most strongly reducing ligand, PAA6Me, copper(I) derivatives were formed even in methanol.

The reduction of copper(II) during reactions of PMK, IMAA and PAA6Me with copper salts requires the presence of a reducing agent. Since nitrogen gas was evolved in all such cases the ligand itself must be the source of the reducing action initially reducing copper(II) to copper(I), which then, by preference, forms a complex with unoxidized ligand. Oxidation products of PAA6Me, IMAA and PMK, other than nitrogen, have, as yet, not been identified, but similar observations have been made by us with certain phthalazine-hydrazone ligands [33] which, from an analysis of the oxidation products, undergo hydrolysis at a hydrazone centre and produce hydrazine, which acts as the reducing agent. In the present study the nitrogen gas released during the redox reactions could result from hydrazine reduction of copper(II) with the hydrazine being produced by hydrolysis of the ligand. Water was present in all solvent media where reductions occurred.

Within the scope of this study, and others [18, 21] involving reactions of hydrazone ligands with copper(II) salts, the ligands PAA, PMK, IMAA and PAA6Me can be placed roughly in the following order of increasing reducing ability; PAA ≤ IMAA < PMK < PAA6Me. Copper(II) chloride derivatives were obtained in all cases using either ethanol or methanol as solvent. Using water as a solvent copper(II) bromide derivatives were obtained with PMK and IMAA (a copper bromide complex of PAA was not reported in Stratton and Busch's earlier work [18]) but with PAA6Me a copper(I) derivative resulted. Although the complex [Cu$_2$(PMK)Br$_4$] was produced in water, reaction of copper(II) perchlorate and PMK in water led to the formation of a copper(I) complex. This is a significant observation and indicates that there is a rather delicate redox balance involved in systems of this sort. This balance is tipped in favour of copper(II) by the presence of the more electronegative, coordinated bromine atoms in **V**. A similar observation can be made with PAA6Me, where, with copper(II) nitrate and copper(II) perchlorate and also with copper(II) bromide in methanol reduction occurs, but in the case of copper(II) chloride no reduction is observed.

There are two factors which appear to be of importance in influencing the outcome of reactions involving PMK, IMAA and PAA6Me; the amount of water present in the solvent and the anion involved. In the case of PAA6Me, although the ligand itself appears to be stable in methanol and ethanol solutions, which contain water, reflecting the relative stability of the azomethine linkage, the presence of the copper(II) ion in such media causes the ligand to hydrolyse in most cases. This effect can be envisaged in terms of an enhancement of the electrophilic nature of the azomethine carbon centre during coordination of an azine nitrogen to a copper(II) ion, which in turn enhances nucleophilic attack at this centre by water. The resulting hydrolysis step presumably produces hydrazine, which acts as the reducing agent, and the parent aldehyde.

In order to test the sensitivity of systems known to reduce in an aqueous environment to the presence of water three reactions were carried out in the solvent mixture methanol/triethylorthoformate (TEOF) which should minimise or eliminate water. Copper(II) perchlorate reacted with PMK to produce just a copper(II) derivative, **IV**, which dissolved in aqueous methanol and aqueous acetonitrile with minimal decomposition as indicated by the persistence of the d—d band at 14000 cm^{-1} found in the nitromethane spectrum. Under similar conditions PAA6Me reacted with copper(II) bromide to produce, as an initial product, compound **XII**, the reduced species, but on standing a green crystalline material **XIII** was obtained from the mother liquor which was shown to be a copper(II) derivative. Reaction of PAA6Me and copper(II) perchlorate in refluxing methanol/TEOF led to the formation of the reduced species **XI**, with

no evidence for the formation of a copper(II) derivative. The formation of copper(I) species in both reactions with PAA6Me reflects the extreme sensitivity of this ligand to even small amounts of water in the presence of the copper(II) ion and the apparent inability of TEOF to completely dry the solvent.

In all cases where copper(I) complexes formed unoxidized ligand is involved. This is probably a reflection on the stability of the copper(I) complex of any potential ligand derived from the hydrolysis of the parent ligand itself. The hydrolysis of such systems would probably produce just monodentate ligands, which would not compete favourably with the hydrazone ligands, which are potentially tetradentate. The hydrolysis reactions must therefore proceed to such an extent that only enough reducing agent is produced to generate as much copper(I) as is required by the remaining unoxidised ligand. Assuming that four electrons are released when hydrazine acts as a reducing agent ($N_2H_{4(aq)} + 4OH_{(aq)}^- \rightarrow N_{2(g)} + 4H_2O + 4e^-$) and that a 1:1 copper(I) complex is formed, then only one fifth of the original ligand would decompose by hydrolysis. That this is so is supported by the fact that when a copper(II) complex is stabilised by initially removing water, the system is then unaffected by the presence of water.

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