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Silver Derivatives of Various Bis(pyrazol-1-yl)alkanes: Their Behaviour in Solution and X-ray Crystal Structure of [{$Me_2C(pz)_2$}$_2$Ag]ClO_4

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Abstract

Various bis(pyrazol-1-yl)alkanes, $(pz)_2CR_2$ (R = Me and pzH = pyrazole; R = H, pzH = pyrazole, 3,5-dimethylpyrazole or 4-nitropyrazole (L^3)), give 1:1 adducts with silver(I) nitrate or methanesulphonate and 2:1 adducts with silver perchlorate or fluoroborate. In [{$Me_2C(pz)_2$}$_2$Ag]ClO_4 four coordination is found but rarely tetrahedral because of the steric misfit of the ligand which forms N–Ag–N angles of 82.6 or 83.8(1)°; the Ag–N distances range from 2.247 to 2.432(4) Å. In solution, according to combined evidence from spectra (^1H and ^{13}C), conductivity and molecular weight determinations, the $(pz)_2CR_2$ ligand is not displaced by acetone, is partially displaced by dimethyl sulphoxide or, in the case of $(L^3)_2AgNO_3$, by nitrate, in agreement with the peculiar behaviour of L^3.

Introduction

Interest towards the coordinating behaviour of bis(pyrazol-1-yl)alkanes, a family of stable and flexible ligands, has been growing, as can be seen from a recent review [1]. Nevertheless, there had been no systematic study on the derivatives of this class of ligands with typical elements, so that an investigation into this area was begun, and, after working on zinc, cadmium, mercury, tin and organotin derivatives [2], the results concerning the interaction between silver(I) and various bis(pyrazol-1-yl)alkanes, $(pz)_2CR_2$, and the behaviour in solution of the complexes obtained as well as the X-ray crystal structure determination on one of them are reported here.

Results and Discussion

The bis(pyrazol-1-yl)alkanes, $(pz)_2CR_2$ or N-N, chosen for this work include the simplest form, bis(pyrazolyl)methane (L^1: pzH = pyrazole, R = H), as well as derivatives having increasing steric hindrance due to alkyl groups near the donor centers (L^2: pzH = 3,5-dimethylpyrazole, R = H; L^5: pzH = 3,5-di-tert-butylpyrazole, R = H); furthermore, the effect of alkyl substituents on coordination was tested by putting two methyl groups on the bridgehead carbon (L^4: pzH = pyrazole, R = methyl), while introduction of a strong electron-withdrawing substituent on the pyrazole ring affords a weakly donating ligand (L^3: pzH = 4-nitropyrazole, R = H), which up to now has failed to give adducts with the zinc, cadmium, mercury(II), mercury(I), tin, or organotin(IV) acceptors investigated [2].

All the said ligands reacted in ethanol (diethyl ether for **IV**) with two typical silver(I) derivatives, that is perchlorate or nitrate, and in the case of L^1 also with the tetrafluoroborate and the methane sulphonate. With all the ligands but L^5 white, solid, air- and (often) light-stable 1:2 or 1:1 adducts, **I**–**X**, precipitated out of the solution, sometimes only after addition of diethyl ether (**III**, **VIII** and **X**)

$$n(\text{N-N}) + \text{AgX} + z\text{H}_2\text{O} = \text{Ag(N-N)}_n\text{X}\cdot z\text{H}_2\text{O}$$

No.	N-N	X	*n*	*z*
I	L^1	NO_3	1	0
II	L^1	ClO_4	2	0
III	L^1	SO_3Me	1	0
IV	L^1	BF_4	2	1
V	L^2	ClO_4	2	0
VI	L^3	ClO_4	2	0
VII	L^4	ClO_4	2	0
VIII	L^2	NO_3	2	2
IX	L^3	NO_3	2	0
X	L^4	NO_3	1	0

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TABLE 1. Silver derivatives: analytical data

Compound	Melting point (°C)	Yield (%)	Elemental analyses (%)[a]		
			C	H	N
$(L^1)AgNO_3$ (I)	180–185	50	26.38 (26.42)	2.55 (2.52)	22.08 (22.02)
$(L^1)_2AgClO_4$ (II)	115	70	33.31 (33.37)	3.21 (3.18)	22.28 (22.25)
$(L^1)Ag(SO_3CH_3)$ (III)	190	42	27.39 (27.35)	3.18 (3.13)	15.87 (15.95)
$(L^1)_2Ag(BF_4)H_2O$ (IV)	150	75	33.08 (33.02)	3.49 (3.54)	21.98 (22.01)
$(L^2)_2AgClO_4$ (V)	230	75	42.94 (42.87)	5.23 (5.19)	18.25 (18.18)
$(L^3)_2AgClO_4$ (VI)	230	50	24.65 (24.57)	1.80 (1.75)	24.63 (24.57)
$(L^4)_2AgClO_4$ (VII)	145	70	38.64 (38.59)	4.35 (4.29)	20.07 (20.01)
$(L^2)_2AgNO_32H_2O$ (VIII)	195–198	35	43.08 (42.97)	5.80 (5.86)	20.44 (20.51)
$(L^3)_2AgNO_3$ (IX)	170–175	80	25.91 (25.99)	1.86 (1.86)	28.57 (28.66)
$(L^4)AgNO_3$ (X)	142	65	31.30 (31.21)	3.46 (3.47)	20.28 (20.28)

[a] Calculated values in parentheses.

All the adducts contain two moles of ligand when the anion is not a good ligand (perchlorate or fluoborate derivatives); in the latter case they are soluble in acetone and dimethyl sulphoxide (DMSO). On the other hand, when there is only one mole of ligand, the compounds are soluble only in DMSO. They are insoluble in dichloromethane, benzene, ethanol or diethyl ether. They were characterized by analytical data (Table 1), infrared (Table 2) and magnetic resonance spectra (Tables 3 and 4 for carbon and for proton NMR, respectively); additional data on the solution behaviour are provided in Table 5 (conductivities) and Table 6 (molecular weight determinations).

The infrared data (Table 2) show all the bands required by the presence of the pyrazole and of the anion. Amongst the former ones there are always weak vibrations at *c.* 3100 cm^{-1} and others, more intense, between 1500 and 1560 cm^{-1}, which, then, may be taken as diagnostic for the presence of this type of ligand.

The electrical conductivity values (Table 5) show that all the compounds are electrolyte, both in acetone (**IX** excepted) or dimethyl sulphoxide. Then the ratio r between the molecular weight determined by osmometry in acetone (Table 6) and the formula weight lies between 0.4 and 0.6, against the value of 0.5 required for dissociation according to eqn. (1), suggested for the compounds **II** or **X**, and eqn. (2) for **IX**

$$Ag(N\text{-}N)_nX = [Ag(N\text{-}N)_n]^+ + [X]^- \qquad (1)$$

$$Ag(L^3)_2(NO_3) = [Ag(L^3)O_2NO] + (L^3) \qquad (2)$$

$$Ag(N\text{-}N)_nX + y(DMSO) = [Ag(DMSO)_y(N\text{-}N)]^+ + (n-1)(N\text{-}N) + [X]^- \qquad (3)$$

For the same complexes in DMSO the value of r is *c.* 0.3, in agreement with solvation according, for example, to eqn. (3). Solvation by DMSO had been observed repeatedly with other derivatives of these ligands with typical elements [2], so that it seems to be a typical feature of this family of complexes. The combined evidence available for the two L^3 derivatives shows the weakness of this ligand, which is displaced by a modest nucleophile such as nitrate.

The proton (Table 3) and carbon NMR (Table 4) spectra gave additional support to the formulae proposed, ruling out any change of the ligands upon coordination. The presence of only one signal for the CH_2 or the CMe_2 protons (or for the corresponding carbon atoms) in the derivatives of the bis(pyrazol-1-yl)alkanes, L^1–L^4, shows that the boat-shaped six-membered $Ag(N\text{-}N)_2C$ cycle is not rigid: the said nuclei become magnetically equivalent through rapid

TABLE 2. Selected infrared data (cm^{-1})[a]

Compound	ν(C–H) azole	1500–1600[b]	<500	Others
L[1] [c]	3135m	1520m	397s	
	3110m	1510sh	360m	
				NO_3
I	3165w	1525m	423m	1380vs
	3140w		375w	830m
	3130m		325w	
	3110w			
	3010m			
				ClO_4
II	3140w	1530sh	410m	1120–1070vs,br
	3120m	1520s	360w	620s
	3020m		310w	
				SO_3Me
III	3120m	1525w	425m	1205vs
	3110m	1510w	370w	1175vs
	3010m		345w	1040vs
				770vs
				H_2O
IV	3150m	1525sh	410w	3410w,br
	3130m	1520m	370w	B–F
	3040m			1060vs,br
L[2] [d]	3140w	1565sh	475s	
	3100w	1560m	406w	
			360w	
			310m	
			280m	
				ClO_4
V	3140m	1560vs	490m	1090vs,br
	3100w		470m	620s
	3030m		340m	
			330m	
			280w	
				H_2O
VIII	3130m	1560s	490w	3430s, br
	3100w		475w	NO_3
	3030m		340w	1380vs
	3020m		290w	830m
				NO_2
L[3]	3160m	1535s	470w	1320vs
	3140m	1520s	425w	
	3130m		400w	
	3120m			
	3060m			
				NO_2
VI	3140m	1540s	480w	1300s
	3130m	1520s	410w	ClO_4
				1080vs,br
	3020m			620s
				NO_2
IX	3140w	1545s	410w	1300s
	3120w	1520s	260w	NO_3
	3100m			1380s
	3060w			820s
	3040w			
L[4]	3140w	1540w	390sh	
	3120m	1510m	370m	
				ClO_4
VII	3180w	1520sh	380m	1110–1080vs,br
	3150m	1510m	370m	620s
	3130w			
	3110w			
				NO_3
X	3150m	1520sh	400w	1380vs
	3140m	1510m	360w	820s
	3120w			
	3100m			
	3010m			

(continued)

[a] Nujol mull. [b] Nitro group absorption is also found here. [c] Ref. 2b. [d] Ref. 2d.

inversion or breaking of the long Ag–N bonds, which are found in the X-ray crystal structure of **VII**. However, for acetone solutions it should be noted that while the signals due to the protons (or to the carbons) of the methyl groups in the 3- or 5-position of the ring are displaced upon coordination by not more than 0.1 ppm (or 0.3 for ^{13}C), that of the protons of the $(Me)_2C$ group in L^4 are moved 0.38 ppm downfield in compound **VII**: the shift may be explained as due to a long-distance effect of the coordination center on the average of these six methyl protons; the same shift is not evident for the bridgehead carbon, which is shielded by the protons, or for these in DMSO solvent which in the case of **X** was found to give solvation. In agreement with our previous experience [2] with zinc, cadmium, mercury or tin derivatives of this family of ligands, the chemical shifts of the protons of the bis(pyrazol-1-yl)alkanes employed are generally displaced to lower field upon coordination; on the other hand, in the ^{13}C spectra only the ring carbons move downfield upon coordination while the signals due to the CH_2 carbon do not move or move upfield only slightly. In any case, solvation by DMSO does not seem to be complete except in the case of compound **X**, $Me_2C(Pz)_2 \cdot AgNO_3$: for this negligible displacements upon coordination are observed for both the proton and the carbon NMR spectra.

The combined evidence from measurements carried out in solution (molecular weight determinations, conductivity, proton and carbon NMR spectra) gives here a picture which is different from that obtained when other acceptors were considered. Unless sterically hindered ligands such as bis(3,5-di-tert-butylpyrazolyl)methane are used, adducts are formed with all the bis(pyrazolyl)methanes tried.

TABLE 3. Proton NMR data[a]

	Solvent	CH_2	4-CH	3- or 5-CH		Methyl(s)		Note
L^1	acetone	6.54	6.39t (1.8)	7.61d (1.5)	7.98d (1.8)			b, c
L^1	DMSO	6.39	6.28t (1.8)	7.49d (1.4)	7.93d (2.1)			b
I	DMSO	6.68	6.47t (1.7)	7.73d (1.5)	8.18d (2.1)			
II	acetone	6.86	6.46t (1.7)	7.80d (1.5)	8.27d (2.1)			
III	DMSO	6.72	6.44t (1.8)	7.72d (1.6)	8.26d (2.2)			d
IV	acetone	6.67	6.48t (1.9)	7.83d (1.5)	8.29d (2.1)			
L^2	acetone	6.03	5.75s			2.06	2.44	e, c
V	acetone	6.47	6.10s			2.05	2.57	
VIII	acetone	6.44	6.03s			2.05	2.53	f
L^3	acetone	6.73		8.22s	9.03s			
VI	acetone	7.00		8.46s	9.15s			
IX	acetone	6.88		8.33s	9.10s			
L^4	acetone		6.23t (2.0)	7.46d (1.4)	7.55d (2.5)	2.24		
L^4	DMSO		6.30t (1.8)	7.52d (1.3)	7.73d (1.9)	2.23		
VII	acetone		6.48t (1.2)	7.72d (1.1)	8.24d (1.7)	2.62		
X	DMSO		6.34t (1.2)	7.57d (1.3)	7.88d (1.8)	2.28		
L^5	$CDCl_3$	5.92	6.99s			1.21	1.26	

[a] ppm from TMS; J in Hz in brackets; s = singlet, d = doublet, t = triplet; in the columns where no indication is given all the signals are singlets. [b] Ref. 2b. [c] Ref. 3. [d] 2.44s, methyl. [e] Ref. 2c. [f] 2.92s, water.

TABLE 4. ^{13}C NMR data[a]

	Solvent	C-3	C-4	C-5	R_2C	Methyl(s)		Note
L^1	acetone	140.2	106.4	130.1	64.4			b
II	acetone	142.8	107.3	132.2	64.5			
IV	acetone	143.0	107.4	132.5	64.5			
L^2	acetone	147.7	105.8	140.3	59.5	10.5	13.0	c
V	acetone	150.6	106.8	141.9	59.0	10.6	13.3	
L^3	acetone	136.9		131.1	66.6			d
VI	acetone	138.2		132.1	66.4			d
IX	acetone	137.6		131.6	66.5			d
L^4	acetone	140.9	107.5	129.0	77.8	27.4		
VII	acetone	142.5	106.6	129.5	76.4	27.4		
L^1	DMSO	140.1	106.3	130.5	64.4			b, e
I	DMSO	141.5	106.8	131.6	63.8			
III	DMSO	141.3	106.6	131.4	63.7			f
L^2	DMSO	147.1	105.6	140.0	58.9	10.8	13.3	c
VIII	DMSO	149.3	106.3	141.2	58.5	10.6	13.4	
L^3	DMSO	136.8	135.8	131.6	65.8			g
L^4	DMSO	139.1	105.8	127.7	76.3	27.5		
X	DMSO	139.4	105.8	127.9	76.3	27.4		
L^5	$CDCl_3$	159.0	101.9	152.9	66.8	30.5	29.8	h

[a] Chemical shift, ppm from internal TMS. [b] Ref. 2b. [c] Ref. 2c. [d] C4 not observed. [e] Ref. 4. [f] 9.23 Me-SO_3. [g] Ref. 5. [h] CMe_3 at 97.5.

In the case of the very weakly basic bis(4-nitropyrazolyl)methane, L^3, coordination to Ag(I) in spite of a reported basic pK_a of −1.96 for 4-nitropyrazole [3] suggests that π-backdonation is possible through the bond between a pyrazole nitrogen and a metal, in agreement with an additional observation, *i.e.* with Rh(I) another complex of L^3, namely (norbornadiene)(L^3)RhCl [4], is known, while no adduct of L^3 has been isolated with cations where basicity rather than π-backdonation is important in order to form the donor bond, such as zinc, cadmium, mercury(II), mercury(I), tin or organotin(IV) [2].

TABLE 5. Conductivity data[a]

Compound	Solvent	Concentration × 10^{-3} (molar)	Molar conductivity ($ohm^{-1}\ cm^2\ mol^{-1}$)
I	DMSO	1.08	42
II	acetone	1.02	147
	DMSO	0.9	40
III	DMSO	0.98	33
IV	acetone	1.30	150
V	acetone	1.14	147
VI	acetone	0.98	150
VII	acetone	1.04	144
VIII	acetone	1.06	92
	DMSO	1.08	42
IX	acetone	1.00	11
	DMSO	0.86	42
X	DMSO	1.08	42

[a] At room temperature.

X-ray Crystal Structure Determination of VII

The structure of the compound bis[2,2′-bis(pyrazol-1-yl)propane]silver(I) perchlorate with

TABLE 6. Molecular weight determinations by osmometry

Compound	Formula weight (*FW*)	Solvent	Concentration (% wt./wt.)	Molecular weight (*MW*)	*MW*/*FW*
II	503.4	acetone	1.53	277	0.55
		DMSO	1.42	156	0.31
V	615.9	acetone	1.39	355	0.58
VI	683.6	acetone	1.49	259	0.38
VII	559.7	acetone	1.23	295	0.53
VIII	614.4	acetone	1.08	373	0.61
		DMSO	2.29	232	0.38
IX	646.2	acetone	1.04	263	0.41
		DMSO	1.28	177	0.27

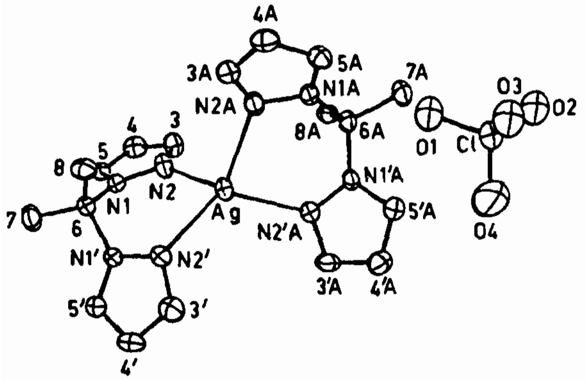

Fig. 1. ORTEP plot and numbering scheme of atoms. Thermal ellipsoids enclose 30% of the electron density.

the numbering scheme, drawn with the program ORTEP [6] is given in Fig. 1. The bond distances and angles are listed in Table 7; selected average values with their standard errors are given in Table 8. The complex exhibits no crystallographic symmetry, though a virtual D_2 symmetry could be guessed. The least-squares planes of the pyrazole rings, and the displacements of atoms from them, with the probability P that the rings are non-planar are given in Table 9. The shortest approach distances between cations or cation and anions x, y, z and the equivalent $1+x, y, z$; $x, y, 1+z$; $1+x, y, 1+z$; $-x, -y, -z$; $-x, -y, 1-z$; $1-x, -y, 1-z$, are normal van der Waals contacts; there are no interanionic contacts shorter than 3.60 Å.

In the coordination sphere the four N–Ag–N angles are 82.6 or 83.1(1)° (inside the chelating ligand) and 104.0–145.1(1)° (outside the chelating ligand); the four Ag–N distances lie in the range 2.247–2.432(4) Å. Clearly, although here Ag(I) is four-coordinated, it is not tetrahedral, in contrast, for example, with the results reported [8] for $[(\text{pyridine})_4\text{Ag}]\text{ClO}_4$ where the Ag–N distance is always 2.322(3) Å and the N–Ag–N angle is either 108.1(1) or 112.3(2)°.

The observed, severe distortion from the expected tetrahedral coordination is probably due to the steric requirements of the 2,2′-bis(pyrazol-1-yl)propane ligand. Although a bis(pyrazol-1-yl)alkane is more flexible than 2,2-bipyridine or phenanthroline, in other of its metal derivatives (listed in ref. 2a) the N–M–N angles actually found are inside the range 71.7(4)–89.0(2)° which includes the values found for **VII**. On one side, a value inside this range may be properly suited in order to accommodate a cation in a planar or octahedral environment, as found, for example, in $[\text{H}_2\text{C}(\text{pz})_2\text{Rh}(\textit{cyclo}\text{-octadiene})]^+$ [4] or $[\text{Me}_2\text{C}(\text{pz})_2]\text{Me}_3\text{PtI}$ [9] where the N–M–N angle is 88.4(3) or 84.7(2)°, respectively. But, on the other hand, values in the same range do not fit well into a tetrahedral coordination: in [bis(3,5-dimethyl-1-pyrazolyl)methane]dicyanomercury(II) N–M–N is 71.7(4) or 79.0(5)°, so that the environment of the mercury atom is hardly tetrahedral in either of the two independent molecules found there [2a], and the Hg–N distances (2.40–2.70(1) Å) give additional evidence of steric misfit of the ligand towards tetrahedral coordination.

In the present compound steric misfit between the two ligands and the potentially tetrahedral silver ion is evidenced not only by effects on the coordination sphere but also by distortion inside the ligands. In an undistorted ligand each of the nitrogen atoms of the pyrazoles is expected to lie in the plane defined by the three neighbouring atoms: indeed this is found for the four nitrogens labelled N1, where the sum of the angles lies between 359.4 and 359.8° (4). But amongst the four atoms labelled N2 the same sum amounts to 358.0, 356.9, 351.6 and 349.6° (4) for N2, N2′A, N2′ and N2A, respectively; in other words, the nitrogen lies in the plane defined by the three immediate neighbours only in the first two cases, while it is out of the plane in the two remaining cases. Correspondingly, there are two sets of N–Ag bonds, one with smaller (N2–Ag and N2′A–Ag, 2.289 and 2.247(4) Å respectively) and one with

TABLE 7. Bond lengths (A) and angles (°) for non-hydrogen atoms

In the coordination sphere			
Ag–N(2)	2.289(4)	Ag–N(2A)	2.432(4)
Ag–N(2′)	2.324(4)	Ag–N(2′A)	2.247(4)
N(2)–Ag–N(2′)	82.6(1)	N(2A)–Ag–N(2′A)	83.8(1)
N(2)–Ag–N(2A)	104.0(1)	N(2′)–Ag–N(2′A)	115.6(1)
N(2)–Ag–N(2′A)	145.1(1)	N(2′)–Ag–N(2A)	135.8(1)
In the ligands			
N(1)–N(2)	1.356(5)	N(1A)–N(2A)	1.362(5)
N(1)–C(6)	1.492(6)	N(1A)–C(6A)	1.498(6)
N(2)–C(3)	1.311(7)	N(2A)–C(3A)	1.309(7)
C(3)–C(4)	1.366(8)	C(3A)–C(4A)	1.359(8)
C(4)–C(5)	1.326(8)	C(4A)–C(5A)	1.384(7)
C(5)–N(1)	1.354(6)	C(5A)–N(1A)	1.319(6)
N(1′)–N(2′)	1.362(5)	N(1′A)–N(2′A)	1.346(5)
N(1′)–C(6)	1.495(6)	N(1′A)–C(6A)	1.471(6)
N(2′)–C(3′)	1.340(7)	N(2′A)–C(3′A)	1.328(7)
C(3′)–C(4′)	1.378(9)	C(3′A)–C(4′A)	1.364(8)
C(4′)–C(5′)	1.360(8)	C(4′A)–C(5′A)	1.348(8)
C(5′)–N(1′)	1.329(6)	C(5′A)–N(1′A)	1.345(6)
C(6)–C(7)	1.527(7)	C(6A)–C(7A)	1.524(6)
C(6)–C(8)	1.515(7)	C(6A)–C(8A)	1.482(7)
N(2)–N(1)–C(5)	109.8(4)	N(2A)–N(1A)–C(5A)	111.4(4)
N(2)–N(1)–C(6)	120.0(3)	N(2A)–N(1A)–C(6A)	119.1(3)
C(5)–N(1)–C(6)	129.7(4)	C(5A)–N(1A)–C(6A)	129.3(4)
Ag–N(2)–N(1)	126.0(3)	Ag–N(2A)–N(1A)	119.5(3)
Ag–N(2)–C(3)	127.6(3)	Ag–N(2A)–C(3A)	125.8(3)
N(1)–N(2)–C(3)	104.4(4)	N(1A)–N(2A)–C(3A)	104.3(4)
N(2)–C(3)–C(4)	112.4(5)	N(2A)–C(3A)–C(4A)	112.8(5)
C(3)–C(4)–C(5)	105.3(5)	C(3A)–C(4A)–C(5A)	104.4(5)
C(4)–C(5)–N(1)	108.1(4)	C(4A)–C(5A)–N(1A)	107.0(4)
N(1)–C(6)–N(1′)	107.0(3)	N(1A)–C(6A)–N(1′A)	108.9(3)
N(1)–C(6)–C(7)	108.0(4)	N(1A)–C(6A)–C(7A)	108.0(4)
N(1)–C(6)–C(8)	110.9(4)	N(1A)–C(6A)–C(8A)	109.4(4)
N(1′)–C(6)–C(7)	108.3(4)	N(1′A)–C(6A)–C(7A)	109.9(4)
N(1′)–C(6)–C(8)	110.9(4)	N(1′A)–C(6A)–C(8A)	110.2(4)
C(7)–C(6)–C(8)	111.6(4)	C(7A)–C(6A)–C(8A)	110.3(4)
N(2′)–N(1′)–C(5′)	110.6(4)	N(2′A)–N(1′A)–C(5′A)	109.7(4)
N(2′)–N(1′)–C(6)	118.2(3)	N(2′A)–N(1′A)–C(6A)	121.5(3)
C(5′)–N(1′)–C(6)	130.6(4)	C(5′A)–N(1′A)–C(6A)	128.6(4)
Ag–N(2′)–N(1′)	123.1(3)	Ag–N(2′A)–N(1′A)	125.7(3)
Ag–N(2′)–C(3′)	125.1(4)	Ag–N(2′A)–C(3′A)	125.0(3)
N(1′)–N(2′)–C(3′)	103.4(4)	N(1′A)–N(2′A)–C(3′A)	106.2(4)
N(2′)–C(3′)–C(4′)	113.4(5)	N(2′A)–C(3′A)–C(4′A)	110.0(5)
C(3′)–C(4′)–C(5′)	102.8(5)	C(3′A)–C(4′A)–C(5′A)	106.4(5)
C(4′)–C(5′)–N(1′)	109.9(5)	C(4′A)–C(5′A)–N(1′A)	107.5(5)
In the perchlorate ion			
Cl–O(1)	1.399(4)	O(1)–Cl–O(3)	106.7(3)
Cl–O(2)	1.369(5)	O(1)–Cl–O(4)	108.4(3)
Cl–O(3)	1.380(5)	O(2)–Cl–O(3)	108.8(3)
Cl–O(4)	1.370(6)	O(2)–Cl–O(4)	106.1(4)
O(1)–Cl–O(2)	113.3(3)	O(3)–Cl–O(4)	113.8(4)

longer distances (N2′–Ag and N2A–Ag, 2.324 and 2.432(4) Å respectively).

The presence of a stronger and weaker Ag–N bond when the donor nitrogen is N2 (or N2′A) and N2′ (or N2A) is supported independently by considering $d' = N1 - N2$, i.e. the difference between the internal angle at N1 and at N2. The value of d' would be zero if the hybridization were the same at N1 as at N2, an

TABLE 8. Average bond distances (Å) and angles (°) with their standard errors[a]

	N	x_m	σ_m	σ'_m
Ag–N	4	2.321	0.040	0.002
N(1)–N(2)	4	1.356	0.004	0.002
N(2)–C(3)	4	1.322	0.007	0.003
C(3)–C(4)	4	1.366	0.004	0.004
C(4)–C(5)	4	1.355	0.012	0.004
C(5)–N(1)	4	1.337	0.008	0.003
N(1)–C(6)	4	1.489	0.006	0.003
C(6)–C(met.)	4	1.513	0.010	0.003
N(2)–Ag–N(2′)	2	83.21	0.58	0.010
N(2)–Ag–N(2A)	2	109.8	5.8	0.1
N(2)–Ag–N(2′A)	2	140.4	4.7	0.1
Ag–N(2)–N(1)	4	123.4	1.5	0.1
Ag–N(2)–C(3)	4	125.9	0.6	0.2
N(1)–N(2)–C(3)	4	104.6	0.6	0.2
N(2)–C(3)–C(4)	4	112.1	0.7	0.2
C(3)–C(4)–C(5)	4	104.8	0.7	0.3
C(4)–C(5)–N(1)	4	108.0	0.6	0.2
C(5)–N(1)–N(2)	4	110.4	0.4	0.2
N(1)–C(6)–N(1′)	2	108.0	1.0	0.2
N(1)–C(6)–C(met.)	8	109.5	0.4	0.1

[a]All values were calculated from ref. 7.

unlikely event here where the first nitrogen is linked with carbon and the second with silver. The value of d' would be different from zero but constant in each ring if only two types of hybridization were present, one for all the N1 atoms and another for all the N2 atoms. Since the values of the four internal angles at N1 lie in such a restricted range (109.7–111.4(4)°) to be considered roughly constant, then the value of d' reflects the difference in the N2 → Ag$^+$ bonds and, not surprisingly, inspection of the values of d', reported below, show that they can be grouped into two sets (3.5, 5.4; 7.1, 7.2), as required:

Angle	d'	d''	$\lvert z \rvert$
N2′A	3.5	3.7	0.6623(5)
N2	5.4	6.7	0.4545(5)
N2A	7.1	7.8	1.1246(5)
N2′	7.2	8.6	0.9543(5)

The differences d', and not the value of the internal angles at N2, must be considered because any change of any internal angle is opposed by the condition that the pyrazole ring must remain planar (i.e. the sum of the angles must be 540°), with the consequent, opposing adjustment of the neighbouring angles. Somewhat different numbers but the same pattern as with d' is obtained with $d'' = (\mathrm{N1} + \mathrm{C3})/2 - (\mathrm{N2})$: this parameter takes into account both the neighbouring angles, those at N1 and at C3. Since both d' and d'' are affected by a rather big e.s.d. (*c.* 0.4°), the existence of two sets of values is more relevant than their numerical values; furthermore, the same two sets are found if $|z|$ is considered, that is the distance (absolute value) between the silver atom and the plane of the pyrazole ring containing the angle indicated (data from Table 9).

As a necessary consequence of the planarity of the pyrazole ring and of the fact that here the internal angle at N1 is always bigger than that at N2, it follows that the internal angle at C3 is bigger than that at C5 and that at C4 is always smaller than C3 and C5. The last point is in agreement with some empirical rules concerning the ground state of pyrazoles [10a] and of various pyrazole derivatives [10b].

The six-membered $C(NN)_2Ag$ rings adopt a boat conformation with the bow at C(6) and the stern at Ag. The puckering parameters [11] are:

in C(6)N(1)N(2)AgN(2′)N(1′) ring

$Q = 0.662 \qquad \theta = 73.2° \qquad \phi = 353.4°$

in C(6a)N(1a)N(2a)AgN(2a′)N(1a′) ring

$Q = 0.634 \qquad \theta = 107.5° \qquad \phi = 174.5°$

These values are to be compared respectively with $\theta = 90°$ and $\phi = 360°$ for an ideal boat, and with $\theta = 90°$ and $\phi = 180°$ for an ideal inverted boat.

The Ag....C(6) and Ag....C(6a) fold angles are 138.0° and 140.9° respectively.

X-ray Analysis

Compound **VII** was crystallized from acetone as colourless prisms. Accurate unit-cell parameters were obtained by a least-squares fit of 2θ values for 25 reflections measured on a Philips PW 1100 computer-controlled single-crystal diffractometer with graphite-monochromated Mo Kα radiation at the Department of Organic Chemistry, University of Padua, Italy; the triclinic cell quoted was confirmed by the use of the TRACER program [12].

The intensities of 5482 independent reflections were collected at room temperature within the angular range $2 \leqslant \theta \leqslant 28°$, using the $\theta/2\theta$ scan technique (scan width = 1.0°, scan speed 0.025° s^{-1}). The intensities of three standard reflections were monitored every 180 min and showed no significant variation. The intensities were corrected for Lorentz and polarization effects and for absorption (minimum and maximum absorption factors 0.9981 and 1.2819) [13]. The structure factors were then placed on an approximate absolute scale by means of a Wilson plot [14].

A total of 2753 reflections having $I \geqslant 3\sigma(I)$ were considered to have observable intensity and used in the structure analysis.

A summary of crystal data is given in Table 10.

TABLE 9. Planarity of molecular regions

	Plane equation[a] χ^2, P	Atoms[b]	Displacements (A)
I	$0.0734X' - 0.7974Y' - 0.5990Z' + 3.1237 = 0$	N(1)*	0.000(4)
		N(2)*	−0.003(4)
		C(3)*	0.009(6)
	$\chi^2 = 4.59$ $(n = 2)$ $P = 89.9\%$	C(4)*	−0.008(6)
		C(5)*	0.003(5)
		C(6)	−0.184(5)
		Ag	0.4545(5)
II	$0.2638X' + 0.0304Y' - 0.9641Z' + 2.5470 = 0$	N(1′)*	0.007(4)
		N(2′)*	−0.007(5)
		C(3′)*	0.001(6)
	$\chi^2 = 16.97$ $(n = 2)$ $P > 99.0\%$	C(4′)*	0.011(6)
		C(5′)*	−0.015(5)
		C(6)	−0.148(5)
		Ag	0.9543(5)
III	$0.1196X' + 0.9011Y' - 0.4169Z' - 2.1895 = 0$	N(1A)*	−0.001(4)
		N(2A)*	0.004(4)
		C(3A)*	−0.008(5)
	$\chi^2 = 4.68$ $(n = 2)$ $P = 90.3\%$	C(4A)*	0.006(5)
		C(5A)*	−0.001(5)
		C(6A)	0.065(5)
		Ag	−1.1246(5)
IV	$0.2569X' + 0.0638Y' - 0.9643Z' + 0.8704 = 0$	N(1′A)*	0.003(3)
		N(2′A)*	−0.009(4)
		C(3′A)*	0.019(6)
	$\chi^2 = 21.93$ $(n = 2)$ $P > 99.0\%$	C(4′A)*	−0.013(6)
		C(5′A)*	0.003(5)
		C(6A)	0.101(4)
		Ag	−0.6623(5)

[a] Transformation matrix from triclinic X, Y, Z to orthogonal X', Y', Z' coordinates:

$$\begin{pmatrix} \sin\gamma & 0 & -\sin\alpha\cos\beta^* \\ \cos\gamma & 1 & \cos\alpha \\ 0 & 0 & \sin\alpha\sin\beta^* \end{pmatrix}$$

[b] Starred (*) atoms were included in the calculation of the plane.

Structure Determination and Refinement

The statistical distribution of the normalized structure factors $E(\langle E\rangle = 0.806$, $\langle E^2 - 1\rangle = 0.911$, $\langle E^3\rangle = 1.519$ and $\langle E^4\rangle = 2.682)$ indicated a centric distribution.

The structure was solved by standard Fourier and Patterson methods. A difference electron density synthesis based upon the Ag signs revealed the positions of all the non-hydrogen atoms. The full-matrix least-squares refinement [15] of the positional and first isotropic and later anisotropic thermal parameters of the non-hydrogen atoms reduced R to 0.055. The positions of the hydrogen atoms were then calculated from the geometry of the compound and checked on a final difference Fourier map. Further refinement, including the hydrogen atoms with the same isotropic thermal parameters of their bonded atoms, reduced R to 0.043 ($R_w = 0.047$). The average shift/e.s.d. ratio in the final refinement cycle was 0.63 in the positional parameters and 0.97 in the thermal parameters of the non-hydrogen atoms. At all stages of the structure analysis, the observed reflections were given unit weights. Attempts to use weights = $\sigma^{-2}(|F_o|)$, made at the end of the refinement, did not lead to better results. The maximum and minimum $\Delta\rho$ values on the final difference Fourier map were 0.31 and −0.39 e Å^{-3} both close to the Ag atom. Anomalous dispersion effects were included in the scattering factors for Ag [12]. No extinction correction was applied. The atomic scattering factors for the non-hydrogen atoms were taken from the International Tables [16] while

TABLE 10. Crystal data, data collection and refinement of the structure

Formula	$C_{18}H_{24}N_8O_4ClAg$
Formula weight	559.78
Space group	$P\bar{1}$
Color	colorless
a (A)	13.292(2)
b (A)	11.625(1)
c (A)	7.5690(6)
α (°)	94.764(6)
β (°)	86.320(6)
γ (°)	102.183(6)
V_c (A^3)	1138.0(2)
Z	2
D_{calc} (g cm^{-3})	1.63
Crystal size (mm)	0.14 × 0.14 × 0.13
μ (Mo Kα) (cm^{-1})	10.25
Data instrument	Philips PW 1100
Radiation (monochromated)	Mo Kα (λ = 0.7107 A)
T of data collection (K)	293
Scan mode	$\theta/2\theta$
Scan speed (° s^{-1})	0.025
Scan width (°)	1.00
Data range (θ)	$2 \leqslant \theta \leqslant 28$
Standards (measured every 300 min)	3 −1 2, −4 3 0, −2 −2 2
No. unique reflections measured	5482 ($\pm h, \pm k, l$)
No. data with $F_o^2 \geqslant 3\sigma(F_o^2)$	2753
No. parameters refined	288
R [a] and R_w [b]	0.043, 0.047
Quality-of-fit indicator[c]	1.46

[a] $R = (\Sigma \| F_o| - k|F_c\|)/(\Sigma |F_o|)$. [b] $R_w = [\Sigma w(|F_o| - k|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = \sigma^{-2}(|F_o|)$. [c] Quality-of-fit $= [\Sigma w(|F_o| - k|F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

TABLE 11. Final coordinates and equivalent isotropic thermal parameters with e.s.d.s in parentheses

Atom	x	y	z	B (A^2)
Non-hydrogen atoms				
Ag	0.05396(3)	0.19633(4)	0.25632(7)	5.25(1)
N(1)	−0.1690(2)	0.2250(3)	0.1250(5)	3.61(1)
N(2)	−0.0655(3)	0.2658(4)	0.1140(6)	5.0(1)
C(3)	−0.0497(4)	0.3293(5)	−0.0242(8)	5.5(2)
C(4)	−0.1393(5)	0.3330(5)	−0.1005(7)	5.1(2)
C(5)	−0.2131(4)	0.2661(4)	−0.0064(6)	3.8(1)
C(6)	−0.2180(3)	0.1608(4)	0.2814(6)	4.0(1)
C(7)	−0.3346(4)	0.1353(6)	0.2646(9)	5.9(2)
C(8)	−0.1867(4)	0.2322(4)	0.4531(6)	4.7(2)
N(1′)	−0.1838(2)	0.0458(3)	0.2701(5)	3.8(1)
N(2′)	−0.0866(3)	0.0460(3)	0.3173(6)	5.2(1)
C(3′)	−0.0842(5)	−0.0688(5)	0.3116(7)	6.3(2)
C(4′)	−0.1758(5)	−0.1417(5)	0.2642(8)	5.5(2)
C(5′)	−0.2369(4)	−0.0640(4)	0.2432(7)	5.0(2)
N(1A)	0.2519(2)	0.3840(3)	0.4336(5)	3.6(1)
N(2A)	0.1483(3)	0.3702(3)	0.4203(5)	4.5(1)
C(3A)	0.1170(4)	0.4186(4)	0.5704(7)	5.0(2)
C(4A)	0.1953(4)	0.4651(4)	0.6786(7)	4.8(2)
C(5A)	0.2823(4)	0.4400(4)	0.5859(6)	4.2(1)
C(6A)	0.3149(3)	0.3424(4)	0.2798(6)	3.6(1)
C(7A)	0.4279(4)	0.3967(5)	0.3092(8)	5.2(2)
C(8A)	0.2834(4)	0.3804(4)	0.1134(7)	4.4(1)
N(1′A)	0.2934(2)	0.2129(3)	0.2728(4)	3.5(1)
N(2′A)	0.2077(3)	0.1438(3)	0.2276(5)	4.8(1)
C(3′A)	0.2215(4)	0.0335(4)	0.2185(7)	5.1(2)
C(4′A)	0.3186(4)	0.0319(5)	0.2653(7)	5.5(2)
C(5′A)	0.3666(4)	0.1455(5)	0.2958(7)	4.9(2)
Cl	0.5245(1)	0.4400(1)	0.5859(2)	4.77(4)
O(1)	0.4385(3)	0.2530(4)	0.7687(6)	7.6(2)
O(2)	0.6124(4)	0.3112(5)	0.6859(8)	13.6(3)
O(3)	0.5367(4)	0.2616(6)	0.9488(6)	12.9(3)
O(4)	0.5072(4)	0.1399(5)	0.6946(8)	15.2(3)

those for hydrogen atoms were from ref. 17. The final atomic positional and isotropic equivalent thermal parameters are given in Table 11.

Supplementary Material

Tables of anisotropic thermal parameters for non-hydrogen atoms, bond distances and angles involving hydrogen atoms, final atomic positional and isotropic thermal parameters for hydrogen atoms and a list of structure factors can be obtained from one of the authors (B. Bovio) on request.

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References

1 S. Trofimenko, *Prog. Inorg. Chem.*, *34* (1986) 115.

2 (a) A. Cingolani, A. Lorenzotti, G. Gioia Lobbia, D. Leonesi, F. Bonati and B. Bovio, *Inorg. Chim. Acta*, *132* (1987) 167; (b) A. Lorenzotti, A. Cingolani, G. Gioia Lobbia, D. Leonesi and F. Bonati, *Gazz. Chim. Ital.*, *117* (1987) 191; (c) D. Leonesi, A. Cingolani, G. Gioia Lobbia, A. Lorenzotti and F. Bonati, *Gazz. Chim. Ital.*, *117* (1987) 491; (d) A. Lorenzotti, A. Cingolani, D. Leonesi and F. Bonati, *Gazz. Chim. Ital.*, *115* (1985) 619; G. Gioia Lobbia, A. Cingolani, D. Leonesi, A. Lorenzotti and F. Bonati, *Inorg. Chim. Acta*, *130* (1987) 203; G. Gioia Lobbia, F. Bonati, A. Cingolani, D. Leonesi and A. Lorenzotti, *J. Organomet. Chem.*, *359* (1989) 21.

3 J. Elguero, Pyrazoles and their benzo derivatives, in A. R. Katritzky and C. W. Rees (eds.), *Comprehensive Heterocyclic Chemistry*, Vol. 5, Pergamon, Oxford, 1984, Ch. 4.04, p. 223, Table 28.

4 L. A. Oro, M. Esteban, R. M. Claramunt, J. Elguero, C. Foces-Foces and F. H. Cano, *J. Organomet. Chem.*, *276* (1984) 79.

5 R. M. Claramunt, H. Hernandez, J. Elguero and S. Julia, *Bull. Soc. Chim. Fr.*, (1983) 5.

6 C. K. Johnson, *ORTEP, Rep. ORNL-3794*, Oak Ridge National Laboratory, TN, U.S.A., 1965.

7 A. Domenicano, A. Vaciago and C. A. Coulson, *Acta Crystallogr., Sect. B, 31* (1975) 221.

8 K. Nilsson and A. Oskarsson, *Acta Chem. Scand., Ser. A, 36* (1982) 605.

9 H. C. Clark, G. Ferguson, V. K. Jain and M. Parvez, *J. Organomet. Chem.*, *270* (1984) 365.

10 (a) F. Bonati and B. Bovio, *J. Crystallogr. Spectrosc. Res.*, accepted for publication; (b) F. Bonati, *Gazz. Chim. Ital.*, *119* (1989) 291.

11 D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, *97* (1975) 1354.

12 S. L. Lawton, R. A. Jacobson, *TRACER*, a cell reduction program, Ames Laboratory, Iowa State University of Science and Technology, Ames, IA, 1965.

13 A. C. T. North, D. C. Phillips and F. C. Mathews, *Acta Crystallogr., Sect. A, 24* (1968) 351.

14 A. J. C. Wilson, *Nature (London), 150* (1942) 152.

15 W. R. Busing, K. O. Martin and H. A. Levy, *ORFLS*, a Fortran crystallographic least-squares program, *ORNL-TM-305*, 1962.

16 *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, U.K., 1974.

17 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, *42* (1965) 3175.