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# SYNTHESIS AND CHARACTERIZATION OF SOME ZINC, CADMIUM AND MERCURY(II) DERIVATIVES OF BIS(4-METHYLPYRAZOL-1-YL) ALKANES

## C. PETTINARI,\* C. SANTINI and D. LEONESI

Dipartimento di Scienze Chimiche, Università degli studi, via S. Agostino 1, 62032 Camerino, Italy

and

## P. CECCHI

Dipartimento ABAC, Università della Tuscia, via S. C. de Lellis, 01100 Viterbo, Italy

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Abstract—The interaction between bis(4-methylpyrazol-1-yl)methane, L, and various  $MX_2$  (M=Zn, X=Cl, Br or I; M=Cd, X=Cl, Br, I or NO<sub>3</sub>; M=Hg, X=Cl, Br, I, CN or SCN) gives the 1:1 adducts [L]MX<sub>2</sub>, which are air- and thermally stable. The ligand also gives 2:1 {[L]<sub>2</sub>Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, [L]<sub>2</sub>Zn(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, [L]<sub>2</sub>Cd(ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, [L]<sub>2</sub>Hg(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>} and 3:1 {[L]<sub>3</sub>Zn(ClO<sub>4</sub>)<sub>2</sub>, [L]<sub>3</sub>Zn(BF<sub>4</sub>)<sub>2</sub>, [L]<sub>3</sub>Zn(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>O, [L]<sub>3</sub>Cd(BF<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, [L]<sub>3</sub>Hg(ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O} adducts with good acceptors. All the complexes have been characterized from analytical and spectral (IR, far-IR, <sup>1</sup>H and <sup>13</sup>C NMR) data. The adduct [L]HgCl<sub>2</sub>, stable in pyridine solution, readily reacts with PPh<sub>3</sub> and 2,2'-bipyridyl (Bipy) to yield (PPh<sub>3</sub>)<sub>2</sub>HgCl<sub>2</sub> and (Bipy)HgCl<sub>2</sub>, respectively. Comparison is made with the results obtained with group 12 derivatives of other poly(azol-1-yl)alkanes.

Bis(pyrazol-1-yl)alkanes are a family of flexible bidentate ligands which have been shown to afford several types of stable metal derivatives.<sup>1</sup>

We have previously described the preparation and characterization of zinc, cadmium, mercury, tin and silver adducts<sup>2</sup> of these bidentate nitrogendonor ligands and it was found that these molecules are often, but not always, chelating while sometimes they are likely to be bridging.

More recently, the interaction of 1,2-bis(pyrazol-1-yl)ethanes with group 12 acceptors was also reported,<sup>3</sup> indicating that these ligands are able to give stable adducts, mercuriated products and also basic salts.

Following up our interest in the chemistry of pyrazole<sup>4</sup> and its derivatives,<sup>5</sup> we decided to extend our research to the synthesis and characterization

of stable group 12 derivatives of bis(4-methylpyrazol-1-yl)methane (abbreviated as L) (Fig. 1), chosen because it is more basic than bis(pyrazol-1yl)methane ( $L^1$ ) and provides a lower steric hindrance than bis(3,5-dimethylpyrazol-1-yl)methane ( $L^2$ ); consequently, it is probably a better ligand with respect to the others previously investigated.

### **EXPERIMENTAL**

The samples for microanalysis were dried *in* vacuo to constant weight (20°C, ca 0.1 Torr). Elemental analyses (C,H,N) were performed in house with a Carlo–Erba model 1106 instrument. The mercury contents of complexes **15–21** were determined with a SpectrAA-10 Varian atomic absorption spectrophotometer. IR spectra were recorded from 4000 to 100 cm<sup>-1</sup> and from 4000 to 600 cm<sup>-1</sup> with a Perkin–Elmer instrument System 2000 FT-IR and a 1600 Series FT-IR instrument,

<sup>\*</sup>Author to whom correspondence should be addressed.



Fig. 1.

respectively. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a VX-300 Varian spectrometer operating at room temperature (300 MHz for <sup>1</sup>H, 75 MHz for <sup>13</sup>C). Melting points were measured on an IA 8100 electrothermal instrument. The electric conductance of the solutions was measured with a Crison CDTM 522 conductimeter at room temperature. The molecular weight determinations were performed at Pascher's Mikroanalytisches Laboratorium, Remagen, F.R.G.

#### Reagents

The ligand bis(4-methylpyrazol-1-yl)methane (L) was prepared according to the literature method.<sup>6</sup> The other chemicals were analytical reagent grade.

Preparation of bis(4-methylpyrazol-1-yl)methanedichlorozinc(II)

Compound 1 precipitated out upon mixing  $ZnCl_2$ (0.14 g, 1.1 mmol), in diethyl ether (20 cm<sup>3</sup>) with bis(4-methylpyrazol-1-yl)methane, L (0.35 g, 2.0 mmol), in the same solvent (20 cm<sup>3</sup>) and recrystallized from chloroform/ether. Compounds 2, 3, 7, 8, 15 and 21 were prepared similarly, while EtOH was used for compounds 4, 10–12 and 17–19. Compounds 9 and 16 were obtained from methanol solutions. The adducts 5, 6 and 14 (50% aqueous cadmium fluoroborate was employed) and 20 were prepared by addition of an ether suspension of the salt to a stirred ether solution of the ligand. Compound 13 was obtained by stirring a solution of cadmium nitrate (0.24 g, 1.0 mmol) in methanol (20 cm<sup>3</sup>) with an ether solution (15 cm<sup>3</sup>) of the ligand (0.35 g, 2.0 mmol).

## Preparation of bis(triphenylphosphine)dichloromercury(II)

Bis(triphenylphosphine)dichloromercury(II) was prepared by adding a tetrahydrofuran solution (20 cm<sup>3</sup>) of PPh<sub>3</sub> (0.52 g, 2 mmol) to a tetrahydrofuran suspension (20 cm<sup>3</sup>) of bis(4-methylpyrazol-1yl)methanedichloromercury(II) (0.45 g, 1 mmmol). After refluxing for 20 min, the clear solution was reduced in volume to *ca* 20 cm<sup>3</sup> in a rotary evaporator. On cooling, a colourless precipitate was formed which was filtered off and washed with ether (15 cm<sup>3</sup>). (2,2'-Bipyridyl)dichloromercury(II) was prepared similarly. The analytical and spectral data of both the complexes are in accordance with those reported in literature.<sup>7,8</sup>

**CAUTION.** The perchlorato derivatives reported in this paper may explode by shock or heating when dry. Small quantities ( $\leq 0.5$  g) of the dry products should be handled with all possible precautions.

#### **RESULTS AND DISCUSSION**

Interaction between various zinc, cadmium and mercury(II) salts and excess ligand in organic solvents (diethyl ether and/or ethanol) produces the compounds 1-21 (listed in Table 1) according to the reaction:

$$n(L) + MX_2 \cdot xH_2O \rightarrow [(L)_n \{MX_2\}] \cdot xH_2O. \quad (1)$$
  
1-21

A 1:1 adduct is always the product from metal halides or pseudo-halides, while a 1:2 or 1:3 adduct is found with good acceptors such as the perchlorate (4, 12 and 20), tetrafluoroborate (5 and 14) and trifluoroacetate (6 and 21) derivatives and also with zinc trifluoromethanesulphonate (7) and nitrate (8).

Various degrees of hydration result from 0.5 in  $[(L)CdCl_2]\cdot 0.5H_2O$  to 3 in  $[(L)_2Zn(NO_3)_2]\cdot 3H_2O$ .

No adduct has been isolated for zinc or cadmium cyanide, fluoride or cadmium sulphate, even when the reaction was performed under more forcing conditions, i.e. strong excess of the ligand and in refluxing solvent.

Reaction of [L]HgCl<sub>2</sub> (15) with triphenylphosphine or 2,2'-bipyridyl occurs in tetrahydrofuran solution, readily affording the products  $(PPh_3)_2$ HgCl<sub>2</sub> and (Bipy)HgCl<sub>2</sub>, respectively, in quantitative yields, thus giving further support to the weakness of the bonding between the group 12 acceptors and our poly(azol-l-yl)alkane ligands.

All the air-stable colourless complexes 1-21 were

identified from analytical data which appear in Table 1, together with the yields. They are generally insoluble in hydrocarbons and in water, but soluble in acetone and DMSO. Compounds 1, 3, 4, 6, 7, 12 and 15-18 are also soluble in methanol and chlorinated hydrocarbons. The solubility of the compounds in acetone was sufficient for conductivity measurements (Table 2), which indicates that the complexes 1-3, 6, 8-11, 13, 15-19 and 21 are not electrolytes, thus ruling out ionic structures such as  $[M(L)_n]^{2+}[X_2]^{2-}$ . All the compounds are electrically conducting when dissolved in DMSO (with the exception of the adducts 1, 9 and 15-19) or in N,Ndimethylformamide (with the exception of 1, 9 and 15-17). This suggests that extensive solvation due to the complexing nature of these solvents takes place according to the pattern:

$$[(L)_n \{MX_2\}] + xS \to [M(S)_x]^{2+} + 2X^- + nL.$$
(2)

In molecular weight determinations (Table 2) performed on the sufficiently soluble derivatives, compounds 1, 2 and 10 are indissociated in acetone solution, whereas in the same solvent the ratio, r, between the vaporimetric molecular weight and the formula weight for compounds 6, 7, 15, 18, 19 and 20 lies in the range 0.44–0.73. This may be due either to ionic dissociation [eq. (2)] or to ligand loss in solution [eq (3)]:

$$[(L)_n \{MX_2\}] + xS \rightarrow [(n-1)L(MX_2) \cdot xS] + L. \quad (3)$$

For complexes 2 and 20, the value of r in DMSO (0.20 and 0.31, respectively) is in reasonable agreement with eq. (2).

#### IR spectra

In the IR spectra (Table 3), the bands typical of the ligand L are easily detected: weak vibrations at ca 3100 cm<sup>-1</sup> and other more intense ones between 1500 and 1600  $\text{cm}^{-1}$ , typical of ring breathing. In the far-IR spectra of complexes 1-3, we assign the two bands at 333 and 314 (compound 1), 257 and 229 (2), 224 and 209 cm<sup>-1</sup> (3) to symmetric and antisymmetric Zn-X stretching modes, respectively. These assignments agree with those previously reported for pseudo-tetrahedral zinc(II) halide complexes with nitrogen-donor ligands such as imidazole<sup>9</sup> or pyridine.<sup>10,11</sup> However, in our case the Zn-N stretching bands cannot be assigned because they are hidden under some ligand absorptions. In the region 200–100  $\text{cm}^{-1}$ , the spectra of 1-3 correspond closely to those of  $Zn(HIm)_2X_2^9$ (where ImH is imidazole). On the basis of this, the strong bands at *ca* 160–180  $\text{cm}^{-1}$  were assigned to the N-Zn-X bending mode. In the derivatives 9-

Table 1. Physical and analytical data of derivatives 1-21

	Compound	M.p.	Yield	Elemental analysis (%); Found (Calc.)							
No.	and formula <sup>a</sup>	(°C)	(%)	С	н	Ň	M				
1	(L)ZnCl <sub>2</sub>	266–269	96	34.3	4.0	17.5					
	$C_9H_{12}Cl_2N_4Zn$			(34.6)	(3.9)	(17.9)					
2	(L)ZnBr <sub>2</sub>	303306	99	26.6	3.0	13.8					
	$C_9H_{12}Br_2N_4Zn$			(26.9)	(3.0)	(14.0)					
3	$(L)ZnI_2$	320 dec.	95	21.8	2.4	11.3					
	$C_9H_{12}I_2N_4Zn$			(21.8)	(2.4)	(11.3)					
4	$(L)_3Zn(ClO_4)_2^b$	266-269	27	40.7	4.8	20.9					
	$C_{27}H_{36}Cl_2N_{12}O_8Zn$			(40.9)	(4.6)	(21.2)					
5	$(L)_3Zn(BF_4)_2$	282-283	18	42.4	5.0	22.2					
	$C_{27}H_{36}B_2F_8N_{12}Zn$			(42.2)	(4.7)	(21.9)					
6	$(L)_3Zn(O_2CCF_3)_2 \cdot H_2O$	113-116	35	44.4	4.7	19.7					
	$C_{31}H_{38}F_6N_{12}O_5Zn$			(44.4)	(4.6)	(20.1)					
7	$(L)_2Zn(CF_3SO_3)_2\cdot 2H_2O$	231-234	86	32.0	3.9	14.5					
	$C_{20}H_{28}F_6N_8O_8S_2Zn$			(31.9)	(3.7)	(14.9)					
8	$(L)_2[Zn(NO_3)_2\cdot 3H_2O$	188190	46	35.9	4.9	23.4					
	$C_{18}H_{30}N_{10}O_9Zn$			(36.3)	(5.1)	(23.5)					
9	$(L)CdCl_2 \cdot 1/2H_2O$	> 370 dec.	30	29.3	3.4	15.0					
	$C_{18}H_{26}Cd_2Cl_4N_8O$			(29.3)	(3.6)	(15.2)					
10	(L)CdBr <sub>2</sub>	272274	20	24.1	2.7	12.1					
	$C_9H_{12}Br_2CdN_4$			(24.1)	(2.7)	(12.5)					
11	(L)CdI <sub>2</sub>	264–265	45	19.9	2.2	10.0					
	$C_9H_{12}CdI_2N_4$			(19.9)	(2.2)	(10.3)					
12	$(L)_2Cd(ClO_4)_2 \cdot H_2O^b$	293–296	45	31.9	4.1	16.3					
	$C_{18}H_{26}CdN_8O_9Cl_2$			(31.7)	(3.8)	(16.4)					
13	$(L)Cd(NO_3)_2$	> 200 dec.	21	25.8	2.9	19.9					
	$C_9H_{12}CdN_6O_6$			(26.2)	(2.9)	(20.4)					
14	$(L)_{3}Cd(BF_{4})_{2}\cdot H_{2}O$	285-288	46	39.2	4.7	20.1					
	$C_{27}H_{38}B_2CdF_8N_{12}O$			(38.9)	(4.6)	(20.2)					
15	(L)HgCl <sub>2</sub>	220-222	98	24.1	2.7	12.4	44.7				
	$C_9H_{12}Cl_2HgN_4$			(24.1)	(2.7)	(12.5)	(44.8)				
16	(L)HgBr <sub>2</sub>	238–239	65	19.9	2.2	10.1	36.6				
	$C_9H_{12}Br_2HgN_4$			(20.1)	(2.2)	(10.4)	(37.4)				
17	(L)HgI <sub>2</sub>	223-224	55	17.2	1.9	8.8	31.4				
	$C_9H_{12}HgI_2N_4$			(17.1)	(1.9)	(8.9)	(31.8)				
18	$(L)Hg(CN)_2$	195–197	28	30.7	2.8	19.3	45.8				
	$C_{11}H_{12}HgN_6$			(30.8)	(2.8)	(19.6)	(46.8)				
19	$(L)Hg(SCN)_2$	159–161	57	26.9	2.4	16.6	41.1				
	$C_{11}H_{12}HgN_6S_2$			(26.8)	(2.4)	(17.0)	(40.7)				
20	$(L)_{3}Hg(ClO_{4})_{2}\cdot H_{2}O^{b}$	207–209	76	33.9	3.8	17.5	21.3				
	$C_{27}H_{38}N_{12}Cl_2O_9Hg$			(34.3)	(4.0)	(17.8)	(21.2)				
21	$(L)_2$ Hg(CF <sub>3</sub> COO) <sub>2</sub>	174–176	82	33.5	3.0	13.9	26.7				
	$C_{20}H_{24}F_6HgN_8O_4$			(33.9)	(3.1)	(14.4)	(25.7)				

<sup>*a*</sup> L is bis(4-methylpyrazol-l-yl)methane,  $C_9H_{12}N_4$ .

<sup>b</sup> See precautions to be used with these compounds.

11 and 15–17, v(M-X) were also identified; the mercury(II) derivatives 15–17 show almost no separation of symmetric and antisymmetric stretching bands.

It has been noted<sup>12a</sup> that IR spectra may be effectively used to distinguish between the uncoordinated and coordinated nitrato groups. The IR spectrum of 8 shows the bands due to unidentate (1457 and 1301 cm<sup>-1</sup>), for which the separation of the two highest frequency (156 cm<sup>-1</sup>) bands is lower than those generally indicated for a bidentate nitrato coordination, and also that due to the uncoordinated nitrato group (1390 cm<sup>-1</sup>).<sup>12</sup> On the other hand, in **13** both the nitrato groups are probably unidentate.

The perchlorato (in the adducts 4, 12 and 20) and

 Table 2. Some molecular weight and conductivity data

		Conductivities <sup>a</sup>					Molecular w	eight <sup>b</sup>
Compound	Solvent	Concentration	Λ	F.w.	M.w.	r	Concentration	on Solvent
1	(CH <sub>3</sub> ) <sub>2</sub> CO	1.2	6.2	312.5	337	1.08	2.83	(CH <sub>3</sub> ) <sub>2</sub> CO
	DMSO	1.3	7.0					
	DMF	1.2	17.6					
2	(CH <sub>3</sub> ) <sub>2</sub> CO	1.0	5.1	401.4	400	1.00	1.36	(CH <sub>3</sub> ) <sub>2</sub> CO
	DMSO	1.0	67.2	401.4	80	0.20	0.86	DMSO
	DMF	1.0	70.0					
3	(CH <sub>3</sub> ) <sub>2</sub> CO	1.0	4.3					
	DMSO	1.2	62.2					
4	$(CH_3)_2CO$	1.0	152.5					
	DMSO	0.9	72.0					
5	(CH <sub>3</sub> ) <sub>2</sub> CO	1.0	137.8					
	DMSO	1.0	91.0					
	DMF	0.7	154.2					
6	(CH <sub>3</sub> ) <sub>2</sub> CO	1.1	8.0	772.7	343	0.44	1.78	$(CH_3)_2CO$
	DMSO	0.8	70.3					
7	(CH <sub>3</sub> ) <sub>2</sub> CO	1.0	130.3	751.2	514	0.68	1.62	$(CH_3)_2CO$
	DMSO	0.9	78.3					
	DMF	1.0	150.4					
8	$(CH_3)_2CO$	1.0	24.2					
	DMSO	1.2	82					
9	(CH <sub>3</sub> ) <sub>2</sub> CO	1.0	9.5					
	DMSO	1.2	9.8					
	DMF	1.3	20.1					
10	$(CH_3)_2CO$	1.1	7.9	448.4	421	0.94	1.56	$(CH_3)_2CO$
	DMSO	1.1	60.5					
11	$(CH_3)_2CO$	1.1	10.6					
	DMSO	1.2	48.8					
12	(CH <sub>3</sub> ) <sub>2</sub> CO	1.0	147.3					
	DMSO	0.9	80.1					
	DMF	1.0	140.0					
13	$(CH_3)_2CO$	1.0	8.7					
	DMSO	0.5	71.3					
14	$(CH_3)_2CO$	1.0	156.9					
	DMSO	1.0	82.4					
15	$(CH_3)_2CO$	1.1	2.2	447.7	315	0.7	2.17	$(CH_3)_2CO$
	DMSO	0.8	4.0					
	DMF	1.2	20.0					
16	$(CH_3)_2CO$	1.0	2.6					
	DMSO	1.0	5.4					
	DMF	1.0	3.2					
17	(CH <sub>3</sub> ) <sub>2</sub> CO	1.0	3.4					
	DMSO	1.1	5.2					
10	DMF	1.3	18.6					
18	$(CH_3)_2CO$	1.0	2.3	428.8	313	0.73	1.68	$(CH_3)_2CO$
	DMSO	0.8	4.5					
10		1.1	90.3	402.0		0.50	1 40	
19	$(CH_3)_2CO$	I.I	4.7	493.0	261	0.53	1.43	$(CH_3)_2CO$
	DMSO	1.0	5.1					
20		1.2	100.5	046.0	607	0.77		
20	$(CH_3)_2CO$	1.0	150.5	946.2	557	0.57	2.35	(CH <sub>3</sub> ) <sub>2</sub> CO
21	DMSO	1.0	/0.7	946.2	305	0.31	1.87	DMSO
<b>41</b>	$(CH_3)_2CO$	1.1	1.2					
	DW2O	1.2	55.5					

<sup>*a*</sup> In  $\Omega^{-1}$  cm<sup>-2</sup> mol<sup>-1</sup> at room temperature; concentration is molar concentration (× 10<sup>3</sup>).

<sup>b</sup> F.w. is the formula weight, M.w. the experimental formula weight, r = F.w./M.w. and concentration is w/w.

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Table 3. Selected ir data  $(cm^{-1})^a$  of adducts 1–21 1600-1500 v(C—H)azole 600 Oth

Compound	v(C—H)azole	1600–1500		< 600		Others					
L	3150m 3085m	1575m	422m 288m	398w 249m	346w						
1	3153w 3122m	1573w	598s	417m	393w	v(ZnCl):333s, 314s					
	3113m 3095w		294m	246w	123m	v(N—Zn—Cl): 184m, 168m					
2	3158w 3114m	1577w	432m	381m	302m	v(Zn-Br):257s, 229s					
	3096w					v(N—Zn—Br): 186m, 172w					
3	3109w 3090w	1575w	431m	381w	300m	v(ZnI): 224s, 209s					
			141m			v(N—Zn—I): 182m					
4	3122w 3092w	1577w	426m	292m	184m	v(ClO <sub>4</sub> ): 1080sbr					
_						624s					
5	3128m 3110w	1577m	528m	425m	290m	v(BF <sub>4</sub> ): 1050sbr					
	<u> </u>	1.697	177m		• • • •	648s, 611s					
6	3161w 3121w	1576m	433w	424w	290w	v(C==O): 1687s, 1430s					
	3085w		270w			v(C-F): 1207s, 1174s, 1135s					
7	2174-2127-	1671-	<b>670</b>	<b>510</b>	40.4	v(O-H): 3300sbr					
/	31/4W 313/W	15/1W	579W	200m	424m	v(O-H): 3400Dr; 1660Dr					
Q	3124w 5100w	1576.	127m	290w 270m	200-	$V(C - \Gamma)$ : 12088, 11708, 10348					
0	J12/11	1370w	427III 260w	370m 107e	166%	V(OH): 5500s0r, 10700r					
			200 ₩	1778	1003	821e					
9	3156w 3123m	1577w	441m	390w	267w	$\nu(OH)$ : 3400whr					
-	3104m	10171	222w	0,000	2011	v(Cd—Cl): 342m. 309m					
10	3138w 3107w	1571w	436m	384m	212m	v(Cd—Br): 255w, 247w					
	3079w		204m	170m		(					
11	3101w 3085w	1569w	437w	390m	300m	v(Cd—I): 231m, 220m					
			258m	175s							
12	3150w 3117m	1580w	430w	421w	299m	v(OH): 3400s br, 1630br					
			254w	240w	152w	v(ClO <sub>4</sub> ): 1080s br, 625s					
13	3162w 3120m	1579w	427m	390w	362w	v(NO <sub>3</sub> ): 1461s, 1305s					
			297m	195sm	150sbr	1019s, 986s, 846m					
14	3157w 3124m	1576w	524s	420s	358w	v(OH): 3540s, 1670br					
	3109m 3036m	1.670	291m	255m	156m	v(BF <sub>4</sub> ): 1066sbr, 640s, 605s					
15	3145w 3107m	1572w	432m	388w	377w	v(HgCl): 318s					
16	3088m	1.570	290m	254w	205						
10	3150W 3104m	1572W	4338	3/8m	295m	v(Hg—Br): 225s					
	508011		255m 114m	18/11	144W						
17	310057 300057	1572.00	114W	383m	207m	u(Hal): 181a					
17	5100w 5090w	1 <i>3</i> /2w	1/3m	11/w	237111	v(11g1). 1815					
18	3116m	1607w	4339	426m	398w	v(C - N): 2200m					
10	STICIL	1576w	321w	297m	278w	v(Hg-C): 120					
		101011	248w	<b>_</b> >/ <b>I</b> I	2701	(11g C). 120					
19	3148w 3108m	1571w	474w	454m	438m	v(SCN): 2131m, 2056w					
			429m	389m	297m	$\delta$ (NCS), 454m, 438m					
			281m	261w	138w						
			119s	281m 261w 119s							
20	3157m 3121m	1575m	440w	380w	424m	v(OH): 3600br, 1628br					
	3097m		298m			v(ClO <sub>4</sub> ): 1079sbr, 624s					
21	3156w 3115m	1588w	519m	439s	412w	v(CO): 1673sbr, 1420s					
	3098m 3027m	1575w	396w	375w	300m	v(CF): 1200s, 1137s					
			265m			10465					

<sup>a</sup> Nujol mull.

the tetrafluoroborato groups (in 5 and 14) were found to be ionic: a single broad absorption at ca1080 cm<sup>-1</sup> and a sharp band at 620 cm<sup>-1</sup> being observed.<sup>13</sup>

The trifluoroacetates **6** and **21** are covalent molecules where the carboxylato ligand is monodentate. In fact, the expected C=O stretching vibration was observed at 1687 (**6**) and 1673 (**21**), respectively, which are similar to the values reported for the two-coordinate (triphenylphosphine) gold(1)trifluoroacetate.<sup>14</sup> The  $\Delta$ [ $\nu_a(CO_2^{-})-\nu_s(CO_2^{-})$ ] values (257 and 253 cm<sup>-1</sup>, respectively) are much greater than those reported for ionic or chelating bidentate complexes.<sup>15</sup>

The IR spectrum of compound **19** exhibits a single sharp absorption near 2131 cm<sup>-1</sup> [ $\nu$ (CN)] and several bands of low intensity due to  $\delta$ (NCS) in the region 450–400 cm<sup>-1</sup>, both typical of thiocyanato S-bonded complexes.<sup>16</sup> In most cases, the bonding mode adopted by the thiocyanate groups in solution is determined by the nature of the solvent. When

the spectrum of **19** is obtained in N,N-dimethylformamide, v(CN) shifts to 2055 cm<sup>-1</sup>: this value could be assigned to the N-bonded thiocyanate group, but in the present case, in view of the conductivity and molecular weight measurements, the shift is probably due to ionic dissociation [eq. (2)].

#### NMR spectra

The <sup>1</sup>H and <sup>13</sup>C NMR spectra, recorded in acetone for all the complexes, are reported in Tables 4 and 5, respectively. In the <sup>1</sup>H spectra, there is generally a downfield displacement upon complexation of all the signals. The difference in chemical shift of a given proton in the complex and in the free ligand,  $\Delta$ , lies between 0.05 and 0.66 ppm; it is observed that  $\Delta$  for the methyl group is always lower than  $\Delta$ for the bridging methylene protons and  $\Delta$  for three or five protons.

In the <sup>13</sup>C spectra the trends of  $\Delta$  are different

Compound <sup>b</sup>	Solvent	CH <sub>3</sub>	CH <sub>2</sub>	3-CH	5-CH	H <sub>2</sub> O
L	(CD <sub>3</sub> ) <sub>2</sub> CO	2.00	6.20	7.26	7.55	
	DMSO	2.00	6.22	7.30	7.67	
1	$(CD_3)_2CO$	2.11	6.79	7.74	8.01	
2	$(CD_3)_2CO$	2.11	6.82	7.76	8.02	
	DMSO	2.00	6.22	7.30	7.67	
3	$(CD_3)_2CO$	2.41	6.86	7.78	8.04	
4	$(CD_3)_2CO$	2.40	6.61	7.35	7.98	
5	$(CD_3)_2CO$	2.05	6.60	7.35	7.98	
6	$(CD_3)_2CO$	2.05	6.52	7.50	7.77	3.02s,br
7	$(CD_3)_2CO$	2.08	6.75	7.54	8.08	3.65s,br, 3.8br
8	$(CD_3)_2CO$	2.08	6.69	7.56	8.04	3.05br
9	$(CD_3)_2CO$	2.03	6.60	7.58	7.81	3.00s
	DMSO	1.99	6.22	7.30	7.68	
10	$(CD_3)_2CO$	2.05	6.75	7.68	7.92	
	DMSO	2.01	6.24	7.30	7.67	
11	$(CD_3)_2CO$	2.08	6.80	7.72	7.96	
12	$(CD_3)_2CO$	2.08	6.78	7.57	8.10	3.15s,br
	DMSO	2.01	6.24	7.30	7.67	
13	$(CD_3)_2CO$	2.09	6.80	7.71	7.96	
14	$(CD_3)_2CO$	2.06	6.70	7.42	8.10	2.90s,br
15	$(CD_3)_2CO$	2.02	6.46	7.40	7.72	
16	$(CD_3)_2CO$	2.02	6.52	7.45	7.80	
	DMSO	2.01	6.24	7.30	7.66	
17	$(CD_3)_2CO$	2.07	6.53	7.42	7.74	
18	$(CD_3)_2CO$	2.00	6.28	7.32	7.60	
19	$(CD_3)_2CO$	2.08	6.60	7.68	7.89	
20	$(CD_3)_2CO$	2.08	6.70	7.60	8.05	4.00s
21	$(CD_3)_2CO$	2.05	6.60	7.54	7.84	

Table 4. <sup>1</sup>H NMR data<sup>a</sup> for complexes 1-21

<sup>*a*</sup>  $\delta$  in ppm from internal TMS.

<sup>b</sup> For the compound extensively dissociated in solution molar, the concentrations are:  $2.3 \times 10^{-2}$  M (2);  $1.5 \times 10^{-2}$  M (9);  $1.7 \times 10^{-2}$  M (10);  $1.3 \times 10^{-2}$  M (12);  $1.6 \times 10^{-2}$  M (16).

Compound	CH <sub>3</sub>	CH <sub>2</sub>	C4	C5	C3
L	9.12	66.13	117.90	129.41	141.68
1	8.83	63.35	119.01	133.23	143.27
2	8.82	63.12	118.98	133.47	143.50
3	8.79	62.79	118.84	133.84	143.73
4	8.96	63.73	118.74	133.41	143.67
5	8.94	63.62	118.67	133.38	143.64
6	9.00	64.89	118.34	131.46	142.96
7	8.90	63.03	118.61	133.66	144.03
8	8.94	63.82	118.68	133.12	143.37
9	7.98	62.20	118.45	131.90	143.80
10	8.93	63.73	118.80	132.37	144.03
11	8.88	63.57	118.67	132.92	144.16
12	8.94	64.00	119.31	134.00	144.55
13	7.61	62.29	117.39	131.66	142.89
14	7.63	62.86	117.98	132.55	142.90
15	7.76	63.65	117.10	129.31	141.14
16	9.00	64.66	118.46	130.95	142.57
17	8.62	64.36	117.91	130.44	142.00
18	7.81	64.39	116.91	128.69	140.83
19	9.04	64.83	118.84	131.92	143.85
20	9.12	65.08	120.12	134.29	144.98
21	7.80	64.50	117.02	129.00	141.01

Table 5. <sup>13</sup>C NMR data<sup>*a*</sup> {(CD<sub>3</sub>)<sub>2</sub>CO} of complexes 1–21

"Chemical shift in ppm from internal TMS.

from those observed in the proton spectra. The  $\Delta$  values are negligible for the methyl carbons and negative for bridging methylene carbons, while they are generally positive for the azole ring carbons, in accordance with an electron flow upon coordination from the N and from the pseudo-aromatic ring of which it is part.

In the <sup>1</sup>H spectra of complexes 2, 9, 10, 12 and 16 in DMSO, the ligand is completely released in solution (the observed signals are almost identical to those obtained from the free ligand solution in DMSO), and this also supports the occurrence of reaction (2) or reaction (3).

Table 6 shows a summary of the interactions of some poly(azol-1-yl)alkanes with various group 12 derivatives.<sup>2,3,17-27</sup>

In the adducts reported, the ligand/metal ratio, n, goes from 0.5 in (L<sup>1</sup>)[ZnCl<sub>2</sub>]<sub>2</sub>·1/2H<sub>2</sub>O<sup>2b</sup>, where the ligand is likely to be bridging, to 3.0 in the ionic [(L)<sub>3</sub>Zn(BF<sub>4</sub>)<sub>2</sub>].

When the ratio, *n*, is 1.5, 2.5 or 5/3 the N–N ligand may be both chelating and bridging. Confimation of the chelating ability of this family of ligands was supplied in the solid state by some X-ray crystal structure determinations performed, for example, on  $[(L^3)Zn(CF_3COO)_2(H_2O)]^{19}$  and  $[(L^4)_2Zn(NO_3)_2]^{.25}$ 

The solubility of the  $L^1$ ,  $L^3$ ,  $L^4$ ,  $L^5$  and  $L^A$  deriva-

tives is limited to a few polar solvents, such as acetone, N,N-dimethylformamide or DMSO, whereas the L,  $L^2$  and  $L^B$  complexes are generally also soluble in chlorinated solvents. This is likely due to the presence of methyl groups.

In a few cases, and only with bis(pyrazol-1-yl) ethanes, the pyrazole ring was metallated or basic salts resulted, while only from the interaction of  $L^B$  with Hg(CN)<sub>2</sub> and Hg(SCN)<sub>2</sub> did breaking of the methylene bridge occur, accompanied by the formation of (pzH)<sub>2</sub>HgX<sub>2</sub> (pzH=3,5-dimethyl-pyrazole, X=CN or SCN).<sup>24</sup>

It has been noted<sup>27</sup> that the ligand L<sup>4</sup>, tris (pyrazol-1-yl)methane, is able to form octahedral compounds and polynuclear complexes owing to the exopolydentate character and can also bind to the same acceptor in more than one way; in fact, the compound  $(L^4)_3(HgCl_2)_5$ , sublimed under vacuum, gave the less volatile molecule  $(L^4)[HgCl_2]_2$  according to the reaction:

 $2(L^4)_3(HgCl_2)_5 \rightarrow L^4 + 5(L^4)[HgCl_2]_2.$ 

The reaction of the poly(azol-1-yl)alkanes with zinc, cadmium and mercury(II) acetate was often unsuccessful, no simple adducts but intractable material being formed, with the exception of  $\{(L^1)[Zn(CH_3COO)_2]_2\}^{2b}$   $\{(L^A)[Zn(CH_3COO)_2]_2\}^{3b}$  and  $[(L^2)Zn(CH_3COO)_2]^{18}$ 

12 salts
l group
s and
)alkane
-1-yl
(azol
poly
various
from
obtained
Compounds
Table 6.

	Ref.	24	24	24		24	24	24	24		24	24	24	24	24	24	24	24	24	24	24		24	24	
	L <sup>a</sup>	1	1	1		1	7	I	7			1	1	-	6	5/3	-	1/2		4	9		J	u	
	Ref.	3b,23	3b	3b,23	3b	3b			3b		3b	3b	3b		3b		3a	3a	3a	За	3a	3a	3a	3a	
	Γ <sup>Α</sup>	-	-	1	1/2	1+			2		1‡	-	1		3‡			-	1	-	-	J	J	q	
	Ref.	22		22		22	22		22	22	22	22	22		22	22	22	22						52	
	٢²	*-		1		7	7		2‡	2§	1	7	6		7	2†	1	7						5*	
	Ref.	21	21	21		21		25	21	21	21	21	21		21	21	27	27					27	27	
	L⁴	1		7		1		7	2*	7	*_	1‡	-		7	7	3/5ª	2/3					3/2	3/2	
(u	Ref.	19,20	19	19		19			19		19	19	19		19		2a						2a		
lar ratio(	Ľ,	-		1		1†			5/2‡		*1		I		2‡		-						l		
Mo	Ref.	17,18	17,18	18	18	18		17	17,18	18	18	18	18		17,18	18	2a			2a			2a	2a	
	$L^2$	-	1	1	1	]*		7	2†	7	1	1	1		2	5/2‡	. –			1			I	7	
	Ref.	2b	2b	2b	2b	2b			2b	2b	2b	2b	2b		2b	2b	26	26	26	26	26	26	26	26	- 4711 - CI
	$\mathbf{L}^{1}$	1/2*	-	1	1/2	. 71			*_	2‡	· <u>*</u> _	7	7		ŝ	5/2		1	-	1	-	I	1	3	5
	Ref.	this work	this work	this work		this work	this work	this work	this work	this work	this work	this work	this work	this work	this work	this work	this work	this work	this work	this work	this work		this work	this work	-
	Ц	-				3†	21	28	, <b>с</b>	ę	*	1	1	1	2†	3†	-	-	-	1	-		7	3†	:
Metal salt	Anion	0	Br	Ι	CH,COO	CF,COO	CF <sub>SO</sub> ,	Ň	CIO	BF.	้อ	Br	Ι	Ň	CIO	BF.	ס	Br	Ι	CN	SCN	CH,COO	CF,COO	CIO	•
	X	Zn	Zn	Zn	Zn	Zn	Zn	Zn	Zn	Zn	Cd	Cd	Cd	Cd	Cd	PC	Ηg	Нg	Hg	Нg	Нg	Чg	Hg	Нg	į

#### Synthesis and characterization of some derivatives of alkanes

<sup>a</sup> These products, sublimed under vacuum, gave (L')[ $HgCl_{2I_2}$ . <sup>b</sup> No adduct formation, but breaking of the C—N bond and consequently the formation of [ $pzHl_{2}HgX_{2}$  (where pzH = 3.5-dimethylpyrazole).

<sup>c</sup> No adduct formation; the 4-position of the pyrazole ring is mercurated.

<sup>d</sup> A basic salt is formed,  $[L^A]_2 \hat{H}g(ClO_4)_2 HgO.$ 

\* No adduct formation; the 4-position of only one pyrazole ring is mercurated. \*+0.5  $H_2O$ . ++1  $H_2O$ . ++2  $H_2O$ . \$+3 $H_2O$ .

With L<sup>5</sup>, and exopolydentate rather than a simply chelating ligand, adducts insoluble in most organic solvents, likely polymeric, are obtained.<sup>25</sup>

The donating ability of this family of ligands can be correlated to the ratio n and to the stability of the complexes in solution. On the basis of this systematic study, L<sup>2</sup>, L<sup>3</sup>, L<sup>A</sup> and L<sup>B</sup> seem to be fair donors since in their compounds, highly dissociated in acetone solution, n is higher than 1 only with good acceptors, such as  $Zn(ClO_4)_2$  or  $Hg(CF_3COO)_2$ . On the other hand, L, L<sup>1</sup>, L<sup>4</sup> and L<sup>5</sup> gave more stable derivatives and sometimes also with a 3:1 ligand/metal ratio.

 $L^2$  and  $L^3$  are weaker donors probably due to the steric hindrance of the methyl groups, whereas the lower donating ability of  $L^A$  and  $L^B$  is due to the fact that chelation requires the formation of a sevenmembered ring. The higher stability of L<sup>4</sup> adducts is due to the fact that it is potentially a tridentate ligand, while the stability of L<sup>5</sup> adducts is probably due to the exopolydentate nature of the donor. L. being more basic than  $L^1$  and having the methyl groups far from the coordination site, seems to be the best ligand among those investigated here, giving more stable adducts and with the highest ligand/metal ratio. However, even in this case, the weakness of the bonding between the nitrogen atoms of L and the group 12 acceptors is demonstrated by the fact that PPh<sub>3</sub> and Bipy easily displaced the ligand from the coordination sphere of the metal centre.

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