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SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF COORDINATION COMPOUNDS OF GROUP 12 METALS CONTAINING THE N_2-DONOR LIGAND BIS(3,4,5-TRIMETHYLPYRAZOL-1-YL)METHANE

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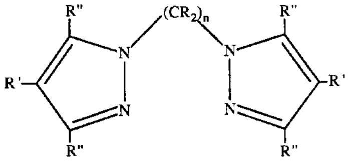
Abstract—The interaction between bis(3,4,5-trimethylpyrazol-1-yl)methane, L^T, and several MX_2 salts, gives 1 : 1 $[L^T]MX_2$ (M = Zn, Cd or Hg; X = Cl, Br or I; M = Zn, X = trifluoroacetate, M = Hg, X = CN, SCN or saccharinate) and 2 : 1 $[L^T]_2MX_2$ adducts (M = Zn, X = NO_3, ClO_4, BF_4, $B(C_6H_5)_4$ or CF_3SO_3; M = Cd, X = NO_3, ClO_4 or BF_4; M = Hg, X = ClO_4) which are air- and thermally stable, while the reaction of L^T with $Hg(CF_3COO)_2$ gives the basic salt $[L^T]Hg(CF_3COO)_2 \cdot 5/4HgO$. The adduct $[L^T]ZnCl_2$ readily reacted with 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one (Q′H), in the presence of a base, to yield the mixed-ligand complex $[L^T(Q')_2Zn]$, whereas $(Q')_2Cd \cdot [H_2O]$ and $(Q')_2Hg \cdot [Et_2O]$ were obtained when a similar reaction was carried out with $[L^T]CdI_2$ and $[L^T]HgCl_2$, respectively, as starting materials. The compound $[L^T]ZnCl_2$ reacted with the anionic pyrazolato ligand (pz^-) and with the neutral 1-methylimidazole (ImH′) yielding the complexes $(pz)_2Zn$ and $(ImH')_2ZnCl_2$, respectively. Displacement of the ligand L^T was observed also from the reaction of $[L^T]CdBr_2$ with 4-phenylimidazole (ImH*) and from the reaction of $[L^T]ZnCl_2$ and $[L^T]ZnBr_2$ with 2,2′-bipyridyl (Bipy), while no interaction was observed with pyridine (py), pyrazole (pzH), 4-bromopyrazole (4-BrpzH) or 3,5-dimethylpyrazole (3,5-Me_2pzH). All the compounds obtained were characterized from analytical and spectral data (IR, far-IR, ^1H and ^{13}C).

Poly(1-pyrazolyl)alkanes (Fig. 1) are a versatile class of neutral nitrogen-donor ligands which form several stable coordination compounds with transition and main-group elements.[1] These stable and flexible bidentate ligands, with a coordination behaviour parallel with those of the isosteric uninegative poly(pyrazolyl)borates,[2] have been reported in the last few years to give metal derivatives which display interesting features. They are often chel-



L: R = R''= H, R' = CH_3, n = 1;
L^1: R = R' = R'' = H, n = 1
L^2: R = R' = H, R'' = CH_3, n = 1;
L^3: R = CH_3, R' = R'' = H, n = 1
L^T: R = H, R' = R'' = CH_3, n = 1,
L^A: R = R' = R'' = H, n = 2
L^B: R = R' = H, R''= CH_3, n = 2

Fig. 1.

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ating and fit into several coordination arrangements[3] and in some cases have been shown to react with various HgX_2 giving either simple adducts or basic salts or mercuriated products.[4] In addition, ligand cleavage of a carbon(sp^3)—nitrogen bond, probably due to an agostic "interaction" M····H—C, has been observed when the reaction between 2,2′-bis(pyrazol-1-yl)propane (L^3) and K_2PtCl_4,[5] $VOCl_2$ or $SnBr_4$[6] in diethyl ether takes place.

In a previous paper[7] we discussed the preparation and characterization of zinc, cadmium and mercury(II) derivatives of bis(4-methylpyrazol-1-yl)methane (L) and also made a comparison with the other results obtained with group 12 derivatives of poly(azol-1-yl)alkanes. Moreover, it has been reported that L, having the methyl group far from the coordination sites, is probably a better ligand with respect to the others so far investigated.

We now describe the synthesis of the related ligand bis(3,4,5-trimethylpyrazol-1-yl)methane (L^T), which is more basic and provides more steric hindrance than L, and also the preparation and properties of its complexes with several zinc, cadmium and mercury(II) acceptors. The reactivity of these new compounds toward several N-donors (Fig. 2), such as imidazole or pyrazole, which are interesting ligands owing to their prominent role in the biological chemistry of transition-metal ions,[8] or toward O-donors, such as the 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone, QH, widely used as extracting agent,[9] has also been investigated. The differences in geometry and in basicity offered by these ligands[10] have been utilized to probe the tendency of likely tetrahedral zinc(II), cadmium(II) and mercury(II) compounds to extend the coordination geometry of the metal centre.

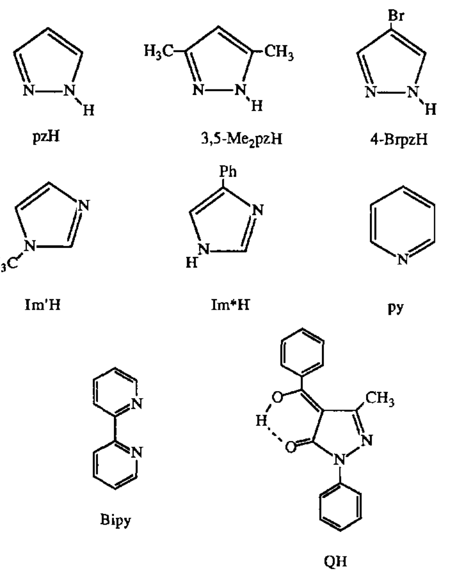

Fig. 2.

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. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin–Elmer System 2000 FT-IR instrument. ^1H and ^{13}C spectra were recorded on a VX-300 Varian spectrometer operating at room temperature (300 MHz for ^1H, 75 MHz for ^{13}C). Melting points were taken on an IA 8100 Electrothermal instrument. The electrical conductance of the solutions was measured with a Crison CDTM 522 conductimeter at room temperature.

Reagents

The ligands bis(3,4,5-trimethylpyrazol-1-yl)methane[11] (L^T) and 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (Q′H)[12] were prepared according to the literature method. Further purification for the former was effected by recrystallization from petroleum ether (m.p. 60–70°C). The other chemicals were analytical reagent grade.

Preparation of bis(3,4,5-*trimethylpyrazol*-1-*yl*) *methanedibromozinc*(II)

Compound **2** precipitated out upon mixing $ZnBr_2$ (0.22 g, 1.0 mmol) in diethyl ether (20 cm^3) with bis(3,4,5-trimethylpyrazol-1-yl)methane, L^T (0.46 g, 2.0 mmol), in the same solvent (30 cm^3) and recrystallized from dichloromethane/ether. Compounds **1**, **3**, **4**, **7**, **17–18** and **24** were prepared similarly, while EtOH was used for compounds **5**, **6**, **11–13** and **19–22**. The adducts **8**, **14**, **15** and **16** (50% aqueous cadmium fluoroborate was employed) were prepared by addition of a diethyl ether suspension of the salt to a stirred diethyl ether solution of the ligand.

Preparation of [*di-bis*(3,4,5-*trimethylpyrazol*-1-*yl*) *methanedi*(*tetraphenylboron*)*zinc*(II)]

Compound **9** was prepared by addition of $NaBPh_4$ (0.40 g, 1.2 mmol) to an ethanol solution of compound **4** (0.19 g, 0.26 mmol). A precipitate formed immediately. The mixture was stirred overnight and the precipitate was then filtered off, washed with ethanol (*ca* 20 cm^3) and recrystallized from chloroform/ether.

Preparation of [{*bis*(3,4,5-*trimethypyrazol*-1-*yl*)*methane*}*bis*(1-*phenyl*-3-*methyl*-4-*benzoyl-pyrazolon*-5-*ato*)*zinc*(II)]

Compound **10** was prepared upon mixing L^TZnCl_2, **1** (0.37 g, 1.1 mmol) with a methanol solution of Q′H (0.56 g, 2.0 mmol) containing an equimolar quantity of KOH (0.114 g, 2.0 mmol). The mixture was stirred overnight under reflux, and then evaporated under reduced pressure. The residue was extracted with dichloromethane (3 × 10 cm^3); after evaporating the extract to dryness, the solid residue was crystallized twice from ethanol/diethyl ether (1/2) to yield the analytical sample.

Preparation of bis(3,4,5-*trimethylpyrazol*-1-*yl*)*methanedisaccharinate mercury*(II)

Complex **24** precipitated out upon addition of L^T (0.46 g, 2.0 mmol) to a warm mixture of aqueous solution (60 cm^3) of saccharin (0.37 g, 1.0 mmol) and mercury(II) acetate (0.32 g, 1.0 mmol) and recrystallized from chloroform/diethyl ether.

Preparation of bis(*N-methylimidazole*)*dichlorozinc* (II)

Bis(N-methylimidazole)dichlorozinc(II) was prepared by adding a methanol solution (20 cm^3) of the N-methylimidazole (0.25 g, *ca* 3.0 mmol) to a methanol solution of **1** (0.37 g, 1.0 mmol). After refluxing for 3 h, the clear solution was evaporated and the residue (0.17 g, 0.56 mmol, 21%) washed with 3 × 25 cm^3 of diethyl ether. M.p. 208–212°C. IR (Nujol mull, cm^{-1}): 1570s, 371m, 240s, 220m, 187m; ν(ZnCl): 310s, 288s. Molar conductance in acetone solution (Ω^{-1} cm^2 mol^{-1}): 4.8. Found: C, 32.3; H, 4.2; N, 18.4. Calc. for $C_8H_{12}Cl_2N_4Zn$: C, 32.0; H, 4.0; N, 18.6%; ^1H NMR in $CDCl_3$: 3.75 (CH_3); 6.95 (5-CH), 7.15 (4-CH), 7.96 (2-CH).

(2,2′-Bipyridyl)dichlorozinc(II) and (2,2′-bipyridyl)dibromozinc(II) were prepared similarly and their analytical and spectral data are in accordance with those reported in the literature.[13]

Preparation of bis(4-*phenylimidazole*)*dibromocadmium*(II)

Bis(4-phenylimidazole)dichlorocadmium(II) was prepared by adding a diethyl ether suspension of **11** to a diethyl ether solution of 4-phenylimidazole. The mixture was stirred overnight and the precipitate was then filtered off and washed with diethyl ether (0.13 g, 0.28 mmol, 57%). M.p. 276–278°C. IR (Nujol mull, cm^{-1}): ν(N—H): 3255s, br; ν(C—H): 3146m, 3121w, 3036m; 1588m, 1571m, 497s, 296m, 262w, 192m, 175m. Molar conductance in acetone solution (Ω^{-1} cm^2 mol^{-1}): 11.0. Found: C, 46.3; H, 3.5; N, 12.1. Calc. for $C_{18}H_{16}CdCl_2N_4$: C, 46.6; H, 3.7; N, 11.7%; ^1H NMR in DMSO: 7.22s (2-CH), 7.60 (5-CH), 7.18–7.80 m (phenyl), 12.22s (N—H). ^{13}C in $(CD_3)_2CO$: 124.38, 125.87, 127.56, 129.67, 137.16.

Attempted preparation of [{*bis*(3,4,5-*trimethylpyrazol*-1-*yl*)*methane*}*bis*(1-*phenyl*-3-*methyl*-4-*benzoyl-pyrazolon*-5-*ato*)*cadmium*(II)] *and* [{*bis*(3,4,5-*trimethylpyrazol*-1-*yl*)*methane*}*bis*(1-*phenyl*-3-*methyl*-4-*benzoyl-pyrazolon*-5-*ato*)*mercury*(II)]

Following the procedures outlined above for compound **10**, with **13** and **17** as precursors and Q′H as the ligand, the compounds $Cd(Q')_2 \cdot [H_2O]$ {m.p. 180 dec; IR (Nujol mull, cm^{-1}): ν(OH): 3200br, ν(C—O): 1609s, 1590s; 1570s, 1533s, 1500sh, 550m, 511m, 426m, 398m, 370m, 342m, 285m; molar conductance in acetone solution (Ω^{-1} cm^2 mol^{-1}): 3.2. Found: C, 59.2; H, 4.3; N, 8.1. Calc. for $C_{34}H_{28}CdN_4O_5$: C, 59.6; H, 4.1; N, 8.2%; ^1H NMR in $CDCl_3$: 1.72s (CH_3), 3.42s (H_2O) 6.97–7.72m (phenyl rings)} and $Hg(Q)_2 \cdot [Et_2O]$ were obtained {m.p. 170 dec; IR (Nujol mull, cm^{-1}): ν(C—O): 1672s, 1630s, 1593s; 544m, 508m, 330m; molar conductance in acetone solution (Ω^{-1} cm^2 mol^{-1}): 90.0. Found: C, 55.5; H, 4.2; N, 7.1. Calc. for $C_{38}H_{36}HgN_4O_5$: C, 55.0; H, 4.4; N, 6.8%; ^1H NMR in $CDCl_3$: 2.02s (CH_3), 6.98–7.55m (phenyl rings), 1.21t, 3.48q (Et_2O)}.

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

RESULTS AND DISCUSSION

The interaction between several zinc(II), cadmium(II) or mercury derivatives and bis (3,4,5-trimethylpyrazol-1-yl)methane, L^T, as described in the Experimental Section, readily afforded the corresponding adducts **1**–**8**, **11**–**22** (Table 1) according to the following general equation (1):

$$nL^T + MX_2 \longrightarrow \underset{1\text{–}8,\,11\text{–}22}{(L^T)_nMX_2}. \qquad (1)$$

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**[a]	**8**	**11**	**12**
M	Zn	Zn	Zn	Zn	Zn	Zn	Zn	Zn	Cd	Cd
X	Cl	Br	I	ClO_4	NO_3	BF_4	CF_3COO	CF_3SO_3	Cl	Br
n	1	1	1	2	2	2	1	2	1	1
Compound	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**
M	Cd	Cd	Cd	Cd	Hg	Hg	Hg	Hg	Hg	Hg
X	I	ClO_4	NO_3	BF_4	Cl	Br	I	CN	SCN	ClO_4
n	1	2	2	2	1	1	1	1	1	2

[a] + 1/2 [Et_2O].

A 1 : 1 adduct is always the product in the case of metal halides or pseudohalides, while a 2 : 1 adduct is obtained only with good acceptors such as the metal(II)perchlorate or nitrate. However, in agreement with the steric hindrance of the ligand L^T, no example was found of a 3 : 1 adduct, to be compared with $(L)_3Cd(ClO_4)$,[7] $(L)_3Zn(BF_4)_2$[7] and $(L^1)_3Cd(ClO_4)_2$.[14]

It is worth considering the different reactivity displayed by these compounds: in fact, the methatesis reaction of $(L^T)_2Zn(ClO_4)_2$ with $NaBPh_4$ gave the required compound $(L^T)_2Zn(BPh_4)_2$, **9**, in quantitative yield, whereas no evidence of reaction was observed when $NaBPh_4$ was reacted with L^TZnCl_2.

When a methanol solution of **1** was heated under reflux with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone, Q′H, in the presence of alkali, the compound $[L^T(Q')_2Zn]$, **10**, was precipitated. However, a similar approach for complexes **13** and **17** gave the two derivatives $Cd(Q')_2 \cdot H_2O$ and $Hg(Q')_2 \cdot Et_2O$, respectively:

$$\underset{\mathbf{1}}{(L^T)ZnCl_2} + 2Q'H + 2KOH \xrightarrow{CH_3OH} \underset{\mathbf{10}}{L^TZn(Q')_2} + 2KCl + 2H_2O \qquad (2)$$

$$(L^T)CdI_2 + 2Q'H + 2KOH \xrightarrow{CH_3OH/H_2O} Cd(Q')_2 \cdot H_2O + L^T + 2KI + 2H_2O \qquad (3)$$

$$(L^T)HgCl_2 + 2Q'H + 2KOH \xrightarrow{CH_3OH/Et_2O} Hg(Q')_2 \cdot Et_2O + L^T + 2KCl + H_2O. \qquad (3')$$

With mercury(II) trifluoroacetate in diethyl ether, a basic derivative $(L^T)Hg(CF_3COO)_2 \cdot 5/4HgO$, **23**, with a definite melting point was obtained. Attempts to perform the same reaction in aqueous CF_3COOH resulted in the production of a material of non-stoichiometric composition.

The adduct $(L^T)Hg(C_7H_4NO_3S)_2$, **24**, was isolated by successive additions of an equimolar quantity of L^T to a warm mixture of aqueous solution of saccharin and mercury(II) acetate.

No adduct of L^T was isolated with zinc or cadmium cyanide, fluoride or sulphate, nor with zinc, cadmium or mercury(II) acetate.

All the derivatives **1–24** are colourless air-stable crystalline solids, generally insoluble in hydrocarbon, in methanol and in ethanol, moderately soluble in acetone, and readily soluble in acetonitrile, DMSO and DMF. Compounds **1–3**, **5**, **7**, **8**, **15** and **17–24** are also soluble in chlorinated solvents.

The conductivity measurements show that apart from the 2 : 1 adducts **4–6**, **8**, **14–16** and **22**, all the other complexes are not electrolytes in acetone solution. Adducts **1–3** and **11–13** became electrically conducting when dissolved in DMSO. This behaviour suggests that these compounds in the last solvent undergo extensive solvation according to the pattern:

$$(L^T)_nMX_2 + x\text{DMSO} \longrightarrow [M(DMSO)_x]^{2+} + 2[X]^- + nL^T. \qquad (4)$$

The mercury(II) derivatives **17–21** and **24** are not electrolytes in DMSO.

Compound **1** was also warmed in methanol solution with pzH in the presence of KOH, and in this case afforded the previously well-described $[(pz)_2Zn]$.[15]

$$(L^T)ZnCl_2 + 2pzH + 2KOH \longrightarrow (L^T) + [(pz)_2Zn] + 2KCl + 2H_2O \qquad (5)$$

Table 1. Physical, analytical and conductivity data of derivatives **1**–**24**

		Yield	M.p.	Elemental analysis (%); Found(Calc.)			Conductivities[b]		
Compound and formula[a]	No.	(%)	(°C)	C	H	N	solv.	conc.	Λ
$(L^T)ZnCl_2$	**(1)**	80	>350dec	42.8	5.4	14.9	DMSO	1.08	8.2
$C_{13}H_{20}Cl_2N_4Zn$				(42.3)	(5.4)	(15.2)			
$(L^T)ZnBr_2$	**(2)**	61	>350dec	34.5	4.5	11.9	DMSO	1.04	33.3
$C_{13}H_{20}Br_2N_4Zn$				(34.1)	(4.4)	(12.2)			
$(L^T)ZnI_2$	**(3)**	77	>350dec	28.6	3.8	10.5	acetone	1.01	2.5
$C_{13}H_{20}I_2N_4Zn$				(28.3)	(3.6)	(10.2)	DMSO	1.03	46.4
$(L^T)_2Zn(ClO_4)_2$[c]	**(4)**	90	282–284	42.8	5.6	14.9	acetone	1.04	164.2
$C_{26}H_{40}Cl_2N_8O_8Zn$				(42.8)	(5.5)	(15.4)	DMSO	1.02	83.3
$(L^T)_2Zn(NO_3)_2$	**(5)**	49	264–265	47.6	6.4	21.2	acetone	1.00	61.3
$C_{26}H_{40}N_{10}O_6Zn$				(47.7)	(6.2)	(21.4)			
$(L^T)_2Zn(BF_4)_2$	**(6)**	71	280–281	44.9	6.0	15.6	acetone	1.00	181.2
$C_{26}H_{40}B_2F_8N_8Zn$				(44.4)	(5.7)	(15.9)			
$(L^T)_2Zn(CF_3COO)_2$	**(7)**	78	203–204	40.9	4.3	10.0	acetone	1.06	6.5
$\cdot 1/2[Et_2O]$				(40.6)	(4.8)	(10.0)			
$C_{19}H_{25}F_6N_4O_{4.5}Zn$									
$(L^T)_2Zn(CF_3SO_3)_2$	**(8)**	85	231–233	40.9	4.9	13.2	acetone	1.02	150.4
$C_{28}H_{40}F_6N_8S_2O_6Zn$				(40.6)	(4.8)	(13.5)	DMSO	1.10	71.1
$(L^T)_2Zn(BPh_4)_2$	**(9)**	50	168–171	76.5	7.2	9.3	acetone	0.4	221.1
$C_{74}H_{80}B_2N_8Zn$				(76.1)	(6.9)	(9.6)			
$(L^T)Zn(Q)_2$	**(10)**	68	175–178	66.2	5.6	12.8	acetone	1.04	3.6
$C_{47}H_{46}N_8O_4Zn$				(66.2)	(5.4)	(13.1)	DMSO	1.04	8.7
$(L^T)CdCl_2$	**(11)**	46	302–303	37.8	4.6	13.1	acetone	1.04	6.4
$C_{13}H_{20}CdCl_2N_4$				(37.6)	(4.8)	(13.5)			
$(L^T)CdBr_2$	**(12)**	54	322–323	30.9	4.0	11.0	acetone	0.65	3.3
$C_{13}H_{20}Br_2CdN_4$				(30.9)	(4.0)	(11.1)	DMSO	1.12	43.1
$(L^T)CdI_2$	**(13)**	64	305–307	26.4	3.2	9.0	acetone	1.13	3.2
$C_{13}H_{20}CdI_2N_4$				(26.6)	(3.3)	(9.3)	DMSO	1.10	52.1
$(L^T)_2Cd(ClO_4)_2$[c]	**(14)**	96	>350dec	40.0	5.3	14.3	acetone	1.00	162.2
$C_{26}H_{40}Cl_2N_8O_8Cd$				(40.2)	(5.2)	(14.4)			
$(L^T)_2Cd(NO_3)_2$	**(15)**	37	283–284	44.3	5.9	19.9	acetone	1.04	46.3
$C_{26}H_{40}N_{10}O_6Cd$				(44.5)	(5.7)	(19.9)	DMSO	1.1	79.3
$(L^T)_2Cd(BF_4)_2$	**(16)**	77	>350dec	42.0	5.6	14.6	acetone	1.06	151.2
$C_{26}H_{40}B_2F_8N_8Cd$				(41.6)	(5.3)	(14.9)			
$(L^T)HgCl_2$	**(17)**	70	257–258	31.3	4.0	10.6	acetone	1.06	3.2
$C_{13}H_{20}Cl_2HgN_4$				(31.0)	(4.0)	(11.1)	DMSO	1.02	2.3
$(L^T)HgBr_2$	**(18)**	78	259–262	26.6	3.3	9.1	acetone	1.03	3.2
$C_{13}H_{20}Br_2HgN_4$				(26.3)	(3.4)	(9.4)	DMSO	1.06	2.2
$(L^T)HgI_2$	**(19)**	67	236–237	22.8	3.0	8.2	acetone	1.01	2.0
$C_{13}H_{20}HgI_2N_4$				(22.7)	(2.9)	(8.2)	DMSO	0.98	1.3
$(L^T)Hg(CN)_2$	**(20)**	45	268–270	37.4	4.2	16.9	acetone	1.05	2.4
$C_{15}H_{20}HgN_6$				(37.2)	(4.2)	(17.3)	DMSO	1.13	1.9
$(L^T)Hg(SCN)_2$	**(21)**	67	175–177	33.1	3.7	15.3	acetone	1.11	7.2
$C_{15}H_{20}HgN_6S_2$				(32.8)	(3.8)	(15.3)	DMSO	1.04	1.7
							DMF	0.51	96.2
$(L^T)_2Hg(ClO_4)_2$[c]	**(22)**	48	167–168	36.1	4.7	12.9	acetone	1.04	141.1
$C_{26}H_{40}Cl_2HgN_8O_8$				(36.1)	(4.6)	(12.9)			
$(L^T)Hg(CF_3COO)_2$	**(23)**	57	200dec	22.2	2.1	5.7	acetone	0.5	25.2
$\cdot 5/4HgO$				(22.0)	(2.2)	(6.0)			
$C_{17}H_{20}F_6Hg_{2.25}N_4O_{5.25}$									
$(L^T)Hg(C_7H_4NO_3S)_2$	**(24)**	47	272–273	40.3	3.5	9.9	acetone	1.01	4.3
$C_{27}H_{30}HgN_6O_6S_2$				(40.7)	(3.5)	(10.5)	DMSO	1.01	10.2

[a] L^T is bis(3,4,5-trimethylpyrazol-1-yl)methane, $C_{13}H_{20}N_4$.

[b] In $\Omega^{-1}cm^2mol^{-1}$ at room temperature; conc. is molar concentration (× 10^3).

[c] See precautions to be used with these compounds.

The 1 : 1 adducts $(L^T)MX_2$ did not display any tendency to coordinate further molecules of L^T or of other ligands to afford species such as $(L^T)_2MX_2$, $(L^T)(A)_2MX_2$ (where A = monodentate nitrogen donor) or $(L^T)(A')MX_2$ (A′ = bidentate nitrogen donor). In fact, in consonance with our previous report[7] on the synthesis of metal derivatives of poly-(pyrazol-1-yl)alkanes, compounds **1** and **2** were found to react with 2,2′-bipyridyl (Bipy) giving $(Bipy)ZnCl_2$ and $(Bipy)ZnBr_2$, while the interaction of **1** with N-methylimidazole (ImH′) and of **12** with 4-phenylimidazole (ImH*) proceeded according to the following equations,

$$(L^T)ZnCl_2 + 2ImH' \longrightarrow (ImH')_2ZnCl_2 + L^T \quad (6)$$

$$(L^T)CdBr_2 + 2ImH^* \longrightarrow (ImH^*)_2CdBr_2 + L^T \quad (6')$$

the two adducts $(ImH')_2ZnCl_2$ and $(ImH^*)_2CdBr_2$ being respectively formed. On the other hand **1** and **2** did not react with pyridine, pzH, 3,5-Me$_2$pzH or 4-BrpzH, even when the reaction was carried out in strong excess of the ligand and in refluxing solvent. This behaviour is in agreement with the lower basicity of these nitrogen donor species with respect to imidazole and its derivatives.[16]

IR spectra

The infrared spectra (nujol mull) of compounds **1–24** (Table 2) are in agreement with the formulae given. The bands typical of the ligand L^T are easily detected: absorption of very weak intensity in the region above 3000 cm^{-1} and two bands more intense between 1500 and 1580 cm^{-1} are always observed.[15,17] According to the conductivity data, the perchlorate and the tetrafluoroborate are ionic also in the solid state, a broad absorption at *ca* 1080 cm^{-1} and a single band at *ca* 600 cm^{-1} being observed.[18] The IR spectra of the $M(L^T)_2(NO_3)_2$ (M = Zn or Cd) exhibits the bands (1390–1380 and 1290–1280 cm^{-1}) characteristic of monodentate coordination for both nitrate groups.[19] The trifluoroacetate derivatives **7** and **23** are covalent molecules, whereas the carboxylato ligand is probably monodentate ($\Delta = [\nu_a(CO_2^-) - \nu_s(CO_2^-)] = 257$ for **7** and 236 cm^{-1} for **23**).[20]

The shift of the ν(C=O) absorption band from 1640 cm^{-1} in the free QH[12] to 1610 in complex **10**, and the non-appearance in the spectra of this compound of the broad absorption band due to ν(OH···O) indicates that both the carbonyl groups of the $(Q)^-$ ligand are involved in bonding to zinc through oxygen atoms. On the basis of previous reports on Zn(β-diketonate)$_2$(L) compounds[21] (L = Phen or Bipy) and also by considering our previous results with 4-acyl-5-pyrazolonato ligands,[22] even though structural information is not available, we suggest that the zinc atom is probably in an approximately octahedral environment, as shown in Fig. 3.

The marked reluctance of Hg(II) to form covalent bonds to oxygen is well established. In an effort to clarify the nature of $Hg(Q')_2 \cdot Et_2O$ its IR spectrum was recorded; a very strong and broad C=O stretching frequency was observed at 1670 cm^{-1} and multiple bands around 520 cm^{-1} typical of carbon–mercury stretching frequencies, while there was no evidence supporting the presence of a Hg—O vibration, expected between 400 and 500 cm^{-1} according to Gibson.[23] It is likely that this slightly soluble compound, analogous to "mercury (II) acetylacetonate" synthesized by Bonati,[24] is either a mixture of variable proportions of C-, N- and O-bonded 4-acyl-5-pyrazolone derivatives or an oligomeric molecule in which mono- and bivalent 4-acyl-5-pyrazolones are linked by mercury (II) atoms.

Far-infrared spectra were recorded in order to obtain information about the metal–ligand and metal–halide bonds. The two M—X stretching vibrations IR-active for the pseudotetrahedral complexes **1–3**, **11–13** and **17–19** may be assigned without much ambiguity. These assignments are the same as those of Cornillsen[25] for (imidazole)$_2$MX$_2$ and of Coates[13] for several (Phen)MX$_2$ (Phen = phenanthroline) and (Bipy)MX$_2$ and are in accordance with those previously reported for zinc, cadmium and mercury derivatives of other bis(pyrazol-1-yl)alkane.[7,26]

In the spectra of all the adducts, because they are often overlapped with ligand vibrations, it has been extremely difficult to assign the metal–nitrogen stretching frequencies, which generally serve as a direct measure of the strength of the coordinate bond. However, the data in Table 2 show that the IR spectra of most of our likely pseudotetrahedral compounds have bands of medium to strong intensity in the region 250–270 cm^{-1} which are not present in the spectrum of the free ligand. These bands are similar to those recorded for other zinc(II) halide complexes of nitrogen-donor monodentate or bidentate ligands[13,25–27] and could be attributed predominantly to ν(Zn—N) vibrations and give further support for the coordination of the ligand to the Zn^{2+} ion via the pyrazolyl nitrogen atoms. The bands which appeared in the region 450–350 cm^{-1}, absent in the spectra of the free bis(3,4,5-trimethylpyrazol-1-yl)methane, could be due to slight changes in the geometry or symmetry of L^T ligand upon complexation.

Table 2. Selected IR data (cm^{-1})[a] of compounds **1**–**24**

Compound	ν(C—H)	1600–1500	<600	Others
L^T		1585m, 1575sh	565w, 528w, 516w, 390w, 367w, 282m br, 230m	
1	3027sh	1583m, 1510m	539w, 404vw, 337s, 235m	ν(Zn—Cl) : 328s, 307s, ν(N—Zn—Cl) : 184m, 176m
2	3020sh	1580m, 1511m	572vw, 538w, 398w, 343m, 330m, 296m	ν(Zn—Br) : 256s, 221s, ν(N—Zn—Br) : 176m, 166m
3	3021sh	1579m, 1507m	570w, 536w, 339m, 326w, 296w, 289w, 231m	ν(Zn—I) : 220s, 199s
4	3060sh	1577m, 1515m	570w, 538m, 357m, 300w, 247m, 218m, 180m	$\nu(ClO_4)$: 1080s br, 624s
5	3040sh	1579m, 1507sh	570w, 537m, 367m, 347m, 296m, 251s, 199s	$\nu(NO_3)$: 1390s, 1280s br
6	3059sh	1581m, 1515m	572w, 537m, 518m, 350m, 340m, 300wbr, 240m	$\nu(BF_4)$: 1050s br, 620s
7	3050w	1583m, 1500sh	530m, 522m, 468m, 442m, 415w, 369m, 276s 252s, 192s, 163s	ν(C═O) : 1710, 1453s ν(C—F) : 1200s, 1141s, 1019s, 720s
8	3039w	1576m, 1518m	574m, 535m, 514m, 355mbr, 300w, 249m, 212m	ν(C—F) : 1207s, 1159s, 1052m ; 739s
9	3054w 3034w	1575m, 1519m	552w, 538m, 468m, 366w, 296m br, 256m, 239m	
10	3040sh	1610s, 1594m 1577m, 1500m	543m, 518w, 458w, 418w, 398w, 385w, 375w 352w, 326w, 282s	
11	3021sh	1575m, 1506sh	569w, 534w, 419w, 362w	ν(Cd—Cl) : 264s
12	3015sh	1579m, 1506m	569w, 535w, 408w, 346m, 327sh, 291w	ν(Cd—Br) : 220s, 188s
13	3020sh	1577m, 1505m	569w, 534w, 413w, 332w, 294w, 238m, 154m	ν(Cd—I) : 188m
14	3060sh	1583m, 1507m	569w, 535w, 420w, 373m, 292w, 249m, 186w	$\nu(ClO_4)$: 1120–1050s br, 621s
15	3020sh	1579m, 1505sh	569w, 535m, 361m, 336m, 292m, 247s, 194m	$\nu(NO_3)$: 1380s br, 1290s br
16	3059w	1583m, 1507m	569w, 535m, 516m, 422m, 372m, 349w, 337w 292s, 249s	$\nu(BF_4)$: 1060 sbr, 620s
17	3020sh	1579m, 1505sh	574w, 566w, 529w, 398w, 341m, 237s, 202m,	ν(Hg—Cl) : 319s, 290s, ν(N—Hg—Cl) : 175m
18	3024sh	1579m, 1503sh	571w, 533m, 416w, 361m, 326m, 289m, 237s	ν(Hg—Br) : 214s, 183s
19	3030shbr	1578m, 1500sh	570w, 533m, 410w, 360m, 325m 282m, 247m, 151m, 140m	ν(Hg—I) : 175s
20	3025sh	1576m	572m, 527m, 417s, 340m, 300m, 288s, 267m 233m, 202m, 171m	ν(CN) : 2178w, 2143w
21	3034sh	1573m, 1515m	566m, 536m, 465m, 455m, 434m, 410m, 343w 332m, 271s, 234m, 212s	ν(SCN) : 2110s
22	3053sh	1578m, 1516m	566w, 545m, 530m, 420m, 372s, 345m, 336m 288 mbr, 247s, 180 m br	$\nu(ClO_4)$: 1110s br, 620s
23	3042sh	1580m	570m, 520m, 426m, 385m, 360s, 278s, 238m	ν(C═O) : 1680s br, 1444s, ν(C—F) : 1187s, 1007s
24	3040sh	1590m, 1579m 1511m	598s, 558m, 550m, 538m, 523m, 447m, 417w 391m, 365m, 292m br, 246m, 165m br	ν(C═O) : 1698s, 1674s

[a] Nujol mull.

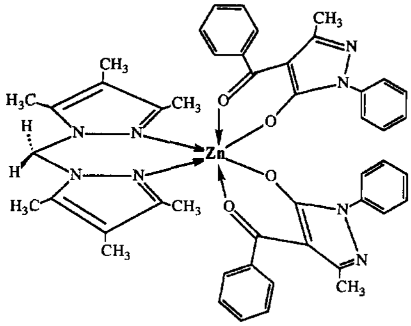

Fig. 3.

The IR spectrum of compound **21** is analogous to that recorded for $(L)Hg(SCN)_2$,[7] a single sharp absorption near 2110 cm^{-1} and several bands of low and medium intensity in the region 400–300 cm^{-1}, both typical of S-bonded thiocyanato, being observed.[28] This complex retains this bonding mode also in acetone solutions [ν(SCN) : *ca* 2105 cm^{-1}], while dissolution of the adducts in DMF invariably results in the "partial" ionization of the coordinated pseudohalide groups, in accordance with the conductivity data.

^{1}H *and* ^{13}C *spectra*

The ^{1}H and ^{13}C NMR spectra (Tables 3 and 4) were recorded for all the complexes isolated (with the exception of ^{13}C spectra for 14 and 16, because of their poor solubility). The choice of the solvent was always dictated by solubility, the order of preference being $CDCl_3$, CD_2Cl_2, $(CD_3)_2CO$ and $(CD_3)_2SO$ (the last solvent has a levelling influence owing to its tendency to displace all the ligands

Table 3. ^{1}H-NMR data[a] for the ligand L^T and complexes **1**–**24**

Compound	Solvent	CH_3			CH_2	Others
L^T	$CDCl_3$	1.83	2.10	2.31	6.03	
	CD_2Cl_2	1.84	2.07	2.34	5.96	
	$(CD_3)_2CO$	1.81	2.01	2.34	6.00	
	DMSO	1.81	2.02	2.32	6.04	
1	CD_2Cl_2	1.90	2.31	2.34	6.22	
	$CDCl_3$	1.90	2.35	2.42	6.28	
	DMSO	1.80	2.02	2.32	6.03	
2	CD_2Cl_2	1.90	2.31	2.34	6.22	
	$(CD_3)_2CO$	1.92	2.35	2.48	6.45	
3	CD_2Cl_2	1.92	2.32	2.40	6.25	
4	$(CD_3)_2CO$	1.78	1.97	2.59	6.70	
5	CD_2Cl_2	1.90	2.40	2.40	6.33	
6	$(CD_3)_2CO$	1.81	1.98	2.59	6.69	
7	$CDCl_3$	1.92	2.23	2.32	6.38	Et_2O : 1.30t, 3.48q
8	$CDCl_3$	1.65	1.90	2.35	6.47	
9	$CDCl_3$	1.80	2.18	2.23	6.54	Q′H : 1.60(CH_3) ; 7.08t, 7.28t, 7.38m, 7.88d (aromatic signals)
10	$(CD_3)_2CO$	1.85	1.99	2.58	6.72	BPh_4 : 6.75t, 6.90t, 7.35m
11	$(CD_3)_2CO$	1.90	2.25	2.48	6.48	
12	$(CD_3)_2CO$	1.93	2.30	2.50	6.51	
13	$(CD_3)_2CO$	1.96	2.35	2.51	6.53	
14	$(CD_3)_2CO$	1.92	2.08	2.53	6.76	
15	CD_2Cl_2	1.90	2.39	2.39	6.28	
16	$(CD_3)_2CO$	1.80	1.90	2.52	6.75	
17	$CDCl_3$	1.88	2.26	2.30	6.28	
18	$CDCl_3$	1.88	2.28	2.30	6.29	
19	$CDCl_3$	1.87	2.29	2.30	6.28	
20	$CDCl_3$	1.87	2.20	2.30	6.08	
21	$CDCl_3$	1.92	2.30	2.33	6.18	
22	$CDCl_3$	1.58	2.30	2.33	6.18	
23	$CDCl_3$	1.90	2.14	2.34	6.34	
24	$CDCl_3$	1.88	2.27	2.32	6.35	$C_7H_4NO_3S$: 7.60–8.00m

[a] δ in ppm from internal TMS.

Table 4. ^{13}C NMR data[a] for the ligand and its complexes **1–24**

Comp.	Solvent	CH_3			CH_2	C(3)	C(4)	C(5)	Others
L^T	CD_2Cl_2	8.47	10.16	12.38	60.92	147.92	113.04	137.36	
	$CDCl_3$	9.48	10.22	12.34	61.42	147.64	113.10	137.33	
	$(CD_3)_2CO$	8.34	10.00	12.33	60.90	147.50	112.75	137.51	
1	CD_2Cl_2	8.18	10.05	12.31	56.69	152.34	114.94	139.24	
2	CD_2Cl_2	7.33	9.19	11.91	55.58	151.75	114.23	138.56	
3	CD_2Cl_2	7.31	9.17	12.87	55.28	152.06	114.37	138.86	
4	$(CD_3)_2CO$	6.75	8.84	10.22	57.24	151.27	114.44	141.81	
5	CD_2Cl_2	8.25	10.17	11.29	57.0br	151.1br	114.85	139.9br	
6	$(CD_3)_2CO$	8.01	10.00	11.47	58.60	152.36	115.62	142.90	
7	$CDCl_3$	8.19	9.91	11.87	56.53	152.59	114.82	139.48	CF_3: 116.75q(288) C=O: 162.93q(37)
8	$CDCl_3$	7.53 7.80	9.52 9.63	10.76	56.66	150.56	114.35	140.01	CF_3: 120.19(315)
9[b]	$CDCl_3$	8.32	9.90	11.99	56.50	150.84	113.85	142.04	
10	$(CD_3)_2CO$	8.04	10.08	11.59	58.63	n.o.	n.o.	n.o.	BPh_4: 122.58, 126.25 126.31
11	$(CD_3)_2CO$	6.85	8.66	11.05	57.73	n.o.	n.o.	n.o.	
12	$(CD_3)_2CO$	8.04	9.91	12.62	58.30	151.80	114.91	140.82	
13	$(CD_3)_2CO$	6.77	8.61	11.89	57.11	n.o.	116.8br	139.5br	
15	CD_2Cl_2	8.34	10.28	11.65	58.46	151.01	114.85	139.70	
17	$CDCl_3$	7.84	9.63	11.84	56.78	149.93	113.80	136.82	
18	$CDCl_3$	7.83	9.62	12.06	56.58	150.07	113.80	136.76	
19	$CDCl_3$	7.81	9.60	12.60	56.51	149.99	113.67	136.65	
20	$CDCl_3$	8.37	10.14	12.56	58.01	149.88	114.06	137.15	CN: 142.67
21	$CDCl_3$	8.47	10.29	12.67	58.17	151.46	114.83	138.50	SCN: 117.90
22	$(CD_3)_2CO$	8.25	10.34	12.07	59.67	152.21	116.18	142.85	
23	$CDCl_3$	7.87	9.65	11.60	57.80	156.26	114.26	138.44	CF_3: 117.4(270) C=O: 161.87(37)
24[c]	$CDCl_3$	8.47	10.23	12.67	57.50	152.16	114.52	138.47	

[a] Chemical shift in ppm from internal TMS; n.o.: not observed due to low solubility.

[b] Q′ signals: 16.91 (3—CH_3); 105.44 (C—4); 149.69 (C—3); 166.66 (C—5); 191.58 (C=O); 121.00, 124.75, 127.87, 128.27, 128.39, 128.82, 130.09, 136.21, 139.65 (Ph).

[c] Saccharinato signals: 120.88, 126.16, 131.52, 133.53, 133.75, 143.49, 165.58.

from the coordination sphere). The spectra of all the compounds show that the ligands have not undergone any structural change upon complexation. In CD_2Cl_2, $CDCl_3$ and acetone solution, all the proton signals shift to lower field upon coordination: this shift, sometimes not negligible, and generally greater in acetone with respect to the chlorinated solvents, could be caused by a change in the electron density of the bis(pyrazol-1-yl)alkane moiety, this fact being consistent with the coordination of the N(2) atom to metal ions.

The metal—(N—N)$_2$C ring is expected in our compounds to be in the boat configuration established through X-ray crystal structure; see, for example, Refs 3 and 29. Consequently, the two N—CH_2—N hydrogens ought to be different: for example, an AB pattern was reported for $(L^1)PtCl_2$,[30] in agreement with the well-established kinetic inertness of platinum(II). However, in all the compounds described here, the N—CH_2—N hydrogen was always found to be magnetically equivalent, at least at room temperature, so that, even when dissociation is not the cause, a rapid boat inversion must be assumed, probably through N—M bond breaking. It has been noted that, in keeping with what has been previously observed,[7,14,26,29] the Δ (= difference in chemical shift of a given proton in the complex with respect to the free ligand) is generally greater in the ionic 2 : 1 complexes than in the 1 : 1 adducts.

In the ^{13}C spectra, the ring and bridging carbon signals move downfield and upfield, respectively, upon complexation, whereas a negligible displacement is observed for the carbon of the three methyl groups. This trend is the same as that already observed with other pyrazol-1-alkanes[28] and (pyrazol-1-yl)borato ligands.[31]

Evidence for an extensive solvation or for a

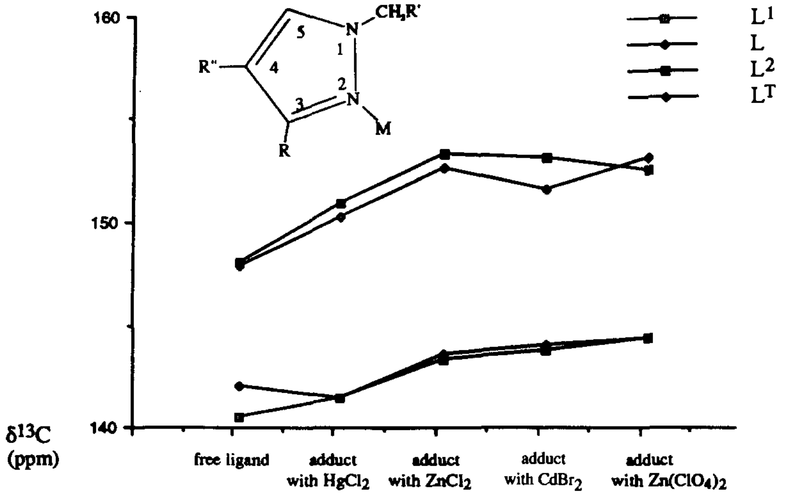

Fig. 4. Graphic of δ ^{13}C resonances (ppm) of 3-C (pyrazole ring) in some bis(pyrazol-l-yl)alkanes and their adducts with mercury(II), zinc and cadmium salts.

ligand dissociation in DMSO is provided also by the proton and ^{13}C NMR spectra. In this solvent the displacement of the carbon or proton signal on going from the free ligand to the ligand in the complexes **1**, **2**, **11**, **13** and **17–19** is negligible.

As far as ^{13}C NMR data are concerned, it seemed interesting to compare the chemical shifts of the 3-C positions in the pyrazole rings in some zinc, cadmium and mercury complexes of several bis (pyrazol-1-yl)alkanes[7,26,29,32] with the corresponding values in the free ligand (Fig. 4). It has been generally observed that changing the ligand does not cause a break in the structural features of the metal derivatives, while changing the metal linked to N(2) causes a different low-field shift of the 3C-resonance: the zinc and cadmium salts, borderline acids, with more bonding affinity for nitrogen-donor ligands,[33] generally produce a higher downfield shift with respect to soft-acid mercury(II) salts.

These results show that the coordination compounds reported here are stable not only in the solid state, but also in chloroform and in acetone solutions. The greater steric hindrance of the more basic L^T, with respect to L, causes a different behaviour: no 3 : 1 adducts were obtained, also under drastic conditions, i.e. strong excess of ligand and refluxing solvent. Easy ligand displacement was observed only with donors with a basic pK_a value of $\sim$6.00, such as 4-phenyl-imidazole (pK_a = 6.10),[16] or with a greater chelating ability, such as 2,2-bipyridyl, whereas it has been observed that pyridine (pK_a = 5.20),[34] only slightly less basic than ImH*, is unable to displace L^T from the metal coordination sphere.

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