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Zinc(II), cadmium(II) and mercury(II) derivatives of bis(4-halopyrazol-1-yl)alkanes: synthesis, spectroscopic characterization and behaviour in solution

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Abstract—The interaction between various bis(4-halopyrazol-1-yl)alkanes L (L^* = bis(3,5-dimethyl-4-chloropyrazol-1-yl)methane, $L^{\#}$ = bis(4-bromopyrazol-1-yl)methane, L° = bis(4-chloropyrazol-1-yl)methane) and zinc(II), cadmium(II) and mercury(II) acceptors gave 1:1 $[LMX_2]$ ($L = L^*$, M = Zn, X = Cl, Br, I, NO_3 or CF_3CO_2; $L = L^*$, M = Cd, X = Cl or Br; $L = L^*$, M = Hg, X = Cl, Br or I; $L = L^{\#}$, M = Zn, X = Cl, Br, I or NO_3; $L = L^{\#}$, M = Cd, X = Cl, Br, I or NO_3; $L = L^{\#}$, M = Hg, X = Cl or Br; $L = L^{\circ}$, M = Zn, X = Cl, M = Cd, X = I, M = Hg, X = Br), 3:2 $[(L^*)_3\{Zn(CF_3SO_3)_2\}_2]\cdot 3H_2O$ and $[(L^*)_3\{Cd(NO_3)_2\}_2]\cdot 2H_2O$, 2:1 $[L_2M]X_2$ ($L = L^*$, M = Zn or Cd, X = ClO_4 or BF_4; $L = L^*$, M = Hg, X = ClO_4; $L = L^{\#}$, M = Zn, X = ClO_4 or CF_3SO_3, M = Cd, X = ClO_4 or BF_4; $L = L^{\circ}$, M = Cd, X = BF_4) and finally 3:1 $[(L^{\#})_3Zn](BF_4)_2$ adducts; these derivatives have been characterized through elemental analyses, spectral data (IR, ^1H and ^{13}C NMR in the case of the sufficiently soluble derivatives), conductivities and molecular weight measurements. Comparison is made with the results obtained with other bis(pyrazol-1-yl)alkanes. © 1997 Elsevier Science Ltd

Keywords: Group 12 derivatives; poly(pyrazol-1-yl)alkanes; ^1H NMR; ^{13}C NMR; IR.

Poly(pyrazol-1-yl)alkanes $[(pz)_nCR_{4-n}]$, a family of stable and flexible neutral polidentate N-donor ligands and especially bis(pyrazol-1-yl)methanes have attracted much attention ever since their discovery [1]. As a result there is a steady stream of new derivatives, because they can be prepared readily and because various substituents may replace each hydrogen atom, so that electronic and steric effects can be varied nearly at will [2].

These molecules form a variety of coordination compounds with main groups and transition metals. Their coordinating behaviour is often very different from that shown by the isosteric uninegative poly(pyrazolyl)borates $[(pz)_nBH_{4-n}]^-$ [3], for which several reviews devoted to their coordination chemistry have been published [4]. On the other hand only limited information has been given on the coordination chemistry of $[(pz)_nCR_{4-n}]$ and at this moment no complete and systematic review has appeared.

Since we have recently discovered that this class of ligands is able to yield stable adducts containing six M–N–N–C–N–N and seven M–N–N–C–C–N–N membered rings [5,6], but also basic salts [7], mercuriated products [7], cleavage of the carbon (sp^3)-nitrogen bond [8] and 'agostic interaction' M···H–C between the metal centre and protons of the bridging methylene groups [9], and then we have realized the importance of the substituents effect of poly(azol-1-yl)alkanes on spectra and structures of the related post-transition metal derivatives, we were prompted by these reports to continue to prepare other $[(pz)_nCR_{4-n}]$ and to study their coordination chemistry towards zinc, cadmium, mercury, tin and silver acceptors. Here we report the synthesis and spectroscopic characterization of 36 new derivatives of Group 12 metals containing bis(4-halopyrazol-1-yl)alkane donors (Fig. 1).

EXPERIMENTAL

The samples for microanalysis were dried *in vacuo* to constant weight (20°C, *ca* 0.1 Torr). Elemental

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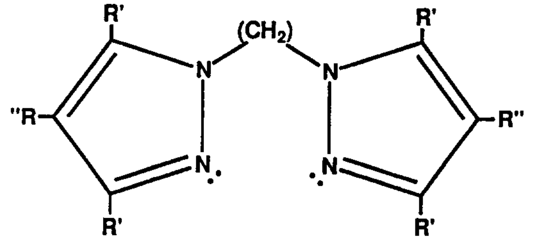

L^*: R' = CH_3, R'' = Cl
$L^\#$: R' = H, R'' = Br
L°: R' = H, R'' = Cl

Fig. 1. Ligands employed in this work

analyses (CHNS) were carried out in the house with a Carlo Erba model 1106 instrument. IR spectra were recorded from 4000 to 100 cm^{-1} and from 4000 to 600 cm^{-1} with a Perkin–Elmer instrument System 2000 FT-IR and a 1600 Series FT-IR instrument, respectively. ^1H-, ^{13}C- and ^{113}Cd NMR spectra were recorded on a VX-300 Varian spectrometer operating at room temperature (300 MHz for ^1H, 75 MHz for ^{13}C, 66.55 MHz for ^{113}Cd). Melting points were taken on an IA 8100 Electrothermal instrument. The electric resistance of solutions was measured with a Crison CDTM 522 conductimeter at room temperature. The osmometric measurements were carried out at 37° over a range of concentrations with a Knauer KNA0280 vapor pressure osmometer calibrated with benzil. The solvent was Baker Analyzed Spectrophotometric grade chloroform or acetone. The results were reproducible to ±2%.

Reagents

Preparation of bis(4-bromopyrazol-1-yl)methane ($L^\#$). The donor bis(4-bromopyrazol-1-yl)methane ($L^\#$) was prepared according to Claramunt's procedure [2b]. The analytical and spectroscopic data of $L^\#$ are in accordance with those reported in literature.

Preparation of bis(3,5-dimethyl-4-chloropyrazol-1-yl)methane (L^*). To a dichloromethane solution (300 cm^3) of 3,5-dimethyl-4-chloropyrazole (10 g, 0.08 mol) (previously prepared from reaction of 3-chloro-2,4-pentanedione with hydrazine hydrate in refluxing ethanol) were added 40 cm^3 of 40% aqueous sodium hydroxide and 0.8 g (2.48 mmol) of tetrabutylammonium bromide. The mixture was vigorously stirred and refluxed during 3 days. The two layers were separated and the aqueous one was extracted with dichloromethane (3 × 100 cm^3). The organic solutions were collected and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure. The residue was recrystallized with hot *n*-hexane (2 × 100 cm^3) to yield 9.0 g of colorless bis(3,5-dimethyl-4-chloropyrazol-1-yl)methane (L^*) (86%) with a melting point of 157–159°C. Calc. for $C_{11}H_{14}Cl_2N_4$: C, 48.4; H, 5.2; N, 20.5%. Found: C, 48.6; H, 5.1; N, 20.3.

Preparation of bis(4-chloropyrazol-1-yl)methane (L°). To a dichloromethane solution (100 cm^3) of 4-chloropyrazole (4.0 g, 0.04 mol) (previously prepared according to Huttel's procedure) [10] were added 20 cm^3 of 40% aqueous sodium hydroxide and 0.4 g (1.24 mmol) of tetrabutylammonium bromide. The mixture was vigorously stirred and refluxed during 4 days. The two layers were separated, the aqueous one was extracted with dichloromethane (3 × 30 cm^3). The organic solutions were collected and then dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure. The residue was recrystallized with hot *n*-hexane (2 × 40 cm^3) to yield 3.0 g of colorless bis(4-chloropyrazol-1-yl)methane (L°) (69%). Calc. for $C_7H_6Cl_2N_4$: C, 38.7; H, 2.8; N, 25.8%. Found: C, 38.4; H, 2.6; N, 26.0.

Preparation of bis(3,5-dimethyl-4-chloropyrazol-1-yl)methanedichlorozinc(II), **1**. Compound **1** precipitated out upon mixing $ZnCl_2$ (0.136 g, 1.0 mmol) in diethyl ether (20 cm^3) with bis(3,5-dimethyl-4-chloropyrazol-1-yl)methane, (L^*) (0.54 g, 2.0 mmol) in the same solvent (20 cm^3) and recrystallized from chloroform/ether. Compounds **2–4**, **14–16**, **18–20**, **31–33** and **36** were prepared similarly, while EtOH was used for compounds **5–7**, **9–12**, **21**, **22**, **24–28**, **30** and **34**.

The adducts **13**, **29**, **35** (50% aqueous cadmium fluoroborate was employed), **8**, **17** and **23** were prepared by addition of an ether suspension of the salt to a stirred ether solution of the ligand.

The analytical and spectral data of the complexes are in accordance with those reported in literature.

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

RESULTS AND DISCUSSION

Reaction of various zinc(II), cadmium(II) and mercury(II) salts with bis(4-halopyrazolyl)alkanes (L in general, in detail: L^*, bis(3,5-dimethyl-4-chloropyrazol-1-yl)methane; $L^\#$, bis(4-bromopyrazol-1-yl)methane; L°, bis(4-chloropyrazol-1-yl)methane take place in organic solvents such as diethyl ether or ethanol, affording the adducts **1–36** according to the reaction (1):

$$nL+mMX_2\cdot yH_2O \xrightarrow{S} [(L)_n\{MX_2\}_m]\cdot yH_2O\cdot zS \tag{1}$$

1 : 1 Adducts were always produced from metal halides, while 2 : 1 or 3 : 1 adducts were found with good acceptors such as the perchlorate and tetrafluoroborate. In this context it is interesting to note that the donor bis(4-bromopyrazol-1-yl)methane, $L^\#$ gives with $Zn(BF_4)_2$ a 3 : 1 adduct, whereas the more basic bis(3,5-dimethyl-4-chloropyrazol-1-yl)methane, L^* gives only a 2 : 1 adduct. The greater steric hindrance of L^* with respect to $L^\#$ causes this different behav-

iour. On the contrary the more basic character due to the four methyl groups may explain why L* gives adducts also with HgI_2 and $HgBr_2$ and why from the reaction between L° and the same acceptors, the starting materials were always recovered.

All the compounds were identified through elemental analyses (Table 1), solid-state infrared spectra (Table 2), conductivity (Table 3), ^1H NMR spectra (Table 4) and in some cases also with molecular weight determinations (Table 3) and ^{13}C NMR spectra (Table 5).

All the compounds are colourless, air- and moisture-stable. The following trends of solubility are observed: all the derivatives **1–36** are insoluble in water, alkanes and alcohols and soluble in DMSO. The zinc(II) and mercury(II) derivatives show appreciable solubility also in chlorinated solvents. The zinc(II)- and cadmium(II)-iodide and -bromide derivatives are more soluble in acetone with respect to the analogous chloride derivatives. In particular, the cadmium(II) chloride adducts **9** and **25** are insoluble in acetone, an observation which suggests a coordination number higher than four through bridging chloride groups. The tetrafluoroborato compounds **7**, **13**, **24**, **29**, **35** are less soluble than the analogous perchlorate **6**, **12**, **22** and **28** derivatives, a feature previously observed also in related $M(BF_4)_2$ compounds [11], for which dimeric structures have been found.

The nitrato and trifluoroacetato zinc(II) and cadmium(II) adducts exhibit the greatest solubility in acetone and chloroform with respect to all the other adducts.

The halide, nitrato and trifluoroacetato adducts are non-electrolytes in acetone solution, thus ruling out self-ionization or displacement of the anion by the solvent, i.e.

$$2[(L)MX_2] \rightarrow [(L)_2M]^{++} + [MX_4]^{=} \qquad (2)$$

$$[(L)_yMX_2] + n\,\text{solvent} \rightarrow [(L)_yM(\text{solvent})_n]^{++} + 2[X]^{-} \qquad (3)$$

In addition, the results of the molecular weight determinations carried out in chloroform for some selected derivatives indicate that a partial displacement of the donor occurs in solution (eq. 4) and that dimerization through a bridging ligand, as previously found in the crystal of {di-[μ-(3,3′-dimethyl-2,2′-biindazole-N1,N1′)]tetrachlorodizinc(II)} ref. [12] should be ruled out. We also noted that dissociation (4) is strongly dependent upon the concentration: for example r (= ratio between the osmometric and calculated molecular weight) for compound **14** is 0.61 at conc. 0.09%.w/w, 0.66 at 0.20%.w/w and finally 0.81 at 0.47%.w/w.

$$[(L)MX_2] \rightleftharpoons (L) + MX_2 \qquad (4)$$

The perchlorato, tetrafluoroborato and trifluoromethanesulfonato derivatives show values of conductivity in acetone, typical of 1 : 1 and 2 : 1 electrolytes. This seems to suggest in acetone solution the existence not only of species such as $[(L)_nM(\text{solvent})_mX]^+[X^-]$, but also $[(L)_nM(\text{solvent})_m]^{++}2[X]^=$.

According to conductivity data, molecular weight determinations indicate for these species the existence of an extensive dissociation such as (5), for example the ratio between the osmometric and the calculated molecular weight for compounds **6** and **12** is *ca* 0.35 at conc. 0.09 and 0.08%. w/w respectively.

$$\begin{aligned}&[(L)_nMX_2] + y\,\text{solvent} \rightleftharpoons [(L)_nM(\text{solvent})_yX]^+\\&+ [X^-] \rightleftharpoons [(L)_{n-1}M(\text{solvent})_yX]^+\\&+ [X^-] + L \rightleftharpoons [(L)_{n-2}M(\text{solvent})_yX]^+\\&+ [X^-] + 2L \rightleftharpoons [(L)_{n-2}M(\text{solvent})_y]^{++} + 2[X^-] + 2L\end{aligned} \qquad (5)$$

IR spectra

In the IR spectra (Table 2), the bands typical of the donor are easily detected: weak vibrations in the range 3050–3150 cm^{-1} {ν(C—H)} and other more intense ones between 1500 and 1600 cm^{-1}, typical of ring breathing, C—H and ring deformation modes at 1300–1000 cm^{-1} [13–15]. In the far-IR spectra of derivatives **1–3**, **18–20** and **33**, we assign the band at *ca* 350 and 320 (**1**, **18** and **33**), 260 and 230 (**2** and **19**), 220 and 200 cm^{-1} (**3** and **20**) to symmetric and antisymmetric Zn—X stretching modes, respectively. As previously found [14,15], substitution of chloride by bromide or iodide shifts the ν(Zn—X) towards lower frequency. The assignments are in accordance with those reported for pseudotetrahedral zinc(halide) complexes containing N-donor ligands such as monodentate imidazoles and bidentate bipyridines [16,17]. In these cases we also note that the absorptions are shifted to higher frequencies with respect to those observed with more basic poly(pyrazol-1-yl)alkanes [18–25]. This indicates a greater weakness of the bonding between the nitrogen atoms of L*, $L^\#$ and L° and the Group 12 acceptors. Further support to this hypothesis is the absence in the region 350–250 cm^{-1} of strong Zn—N stretching bands. In these complexes, these bands, likely of medium intensity, are hidden under weak to medium ligand absorptions. According to Clark and Williams [26], the ν(Zn–Br)/ν(Zn–Cl), ν(Zn–I)/ν(Zn–Cl) and ν(Zn–Br)/ν(Zn–Cl) ratios are in the range 0.73–0.77, 0.63–0.64 and 0.69–0.72 respectively, typical of tetrahedral metal(II)–halide complexes. The ν(Cd–Br)/ν(Cd–Cl) are in the range 0.85–0.93. These values are similar to those reported for distorted polymeric octahedral complexes [26]. In the zinc(II) halide derivatives we also found several strong to medium bands at *ca* 170–200 cm^{-1} likely due to N–Zn–X and/or X–Zn–X bending modes [8,24,25]. The cadmium(II) and mercury(II) adducts exhibit

Table 1. Physical and analytical data of compounds **1**–**36**

		M.p.	Yield	Elem. An. (found %)^b		
Compound	No	(°C)	(%)	C	H	N
$[(L^*)ZnCl_2]$	**1**	319–321	80	32.3	3.6	13.4
$C_{11}H_{14}Cl_4N_4Zn$				32.3	3.4	13.7
$[(L^*)ZnBr_2]$	**2**	318–319	65	27.2	3.0	11.1
$C_{11}H_{14}Br_2Cl_2N_4Zn$				26.5	2.8	11.2
$[(L^*)ZnI_2]$	**3**	300–302	63	22.7	2.5	9.2
$C_{11}H_{14}Cl_2I_2N_4Zn$				22.3	2.4	9.5
$[(L^*)Zn(CF_3COO)_2]$	**4**	226–228	45	31.7	2.8	9.8
$C_{15}H_{14}Cl_2F_6N_4O_4Zn$				31.9	2.5	9.9
$[(L^*)_3\{Zn(CF_3SO_3)_2\}_2] \cdot 3H_2O$	**5**	212–214	93	28.3	3.6	10.8
$C_{37}H_{48}Cl_6F_{12}N_{12}O_{15}S_4Zn_2$				27.8	3.0	10.5
$[(L^*)_2Zn(ClO_4)_2] \cdot 3H_2O^a$	**6**	180–183	92	30.3	3.9	12.7
$C_{22}H_{34}Cl_6N_8O_{11}Zn$				30.6	4.0	13.0
$[(L^*)_2Zn(BF_4)_2]$	**7**	250–255	90	34.3	4.0	14.4
$C_{22}H_{28}B_2Cl_4F_8N_4Zn$				33.7	3.6	14.3
$[(L^*)Zn(NO_3)_2]$	**8**	253–254	63	28.5	3.2	17.6
$C_{11}H_{14}Cl_2N_6O_6Zn$				28.6	3.1	18.1
$[(L^*)CdCl_2]$	**9**	315dec	85	28.2	3.3	11.9
$C_{11}H_{14}CdCl_4N_4$				28.9	3.1	12.3
$[(L^*)CdBr_2]$	**10**	274–276	85	24.0	2.6	10.0
$C_{11}H_{14}Br_2CdCl_2N_4$				24.2	2.6	10.3
$[(L^*)_3\{Cd(NO_3)_2\}_2] \cdot 2H_2O$	**11**	256–257	43	29.1	3.4	16.6
$C_{33}H_{46}CdCl_6N_{16}O_{14}$				29.8	3.5	16.9
$[(L^*)_2Cd(ClO_4)_2]^a$	**12**	310–315	96	31.1	3.5	12.6
$C_{22}H_{28}CdCl_6N_8O_8$				30.8	3.3	13.1
$[(L^*)_2Cd(BF_4)_2] \cdot 2H_2O$	**13**	348dec	98	30.5	3.9	12.4
$C_{22}H_{32}B_2CdCl_4F_8N_8O_2$				30.4	3.7	12.9
$[(L^*)HgCl_2]$	**14**	204–206	45	24.3	2.5	10.8
$C_{11}H_{14}Cl_4HgN_4$				24.3	2.6	10.3
$[(L^*)HgBr_2]$	**15**	208–212	54	21.3	2.4	8.4
$C_{11}H_{14}Br_2Cl_2HgN_4$				20.9	2.2	8.8
$[(L^*)HgI_2]$	**16**	197–199	34	18.4	1.9	7.6
$C_{11}H_{14}Cl_2HgI_2N_4$				18.2	1.9	7.7
$[(L^*)_2Hg(ClO_4)_2]^a$	**17**	224–228	76	27.6	3.1	11.9
$C_{22}H_{28}Cl_6HgN_8O_8$				27.9	3.0	11.8
$[(L^\#)ZnCl_2]$	**18**	289dec	65	19.2	1.4	12.4
$C_7H_6Br_2Cl_2N_4Zn$				19.0	1.4	12.7
$[(L^\#)ZnBr_2] \cdot 1/2H_2O$	**19**	290dec	64	15.8	1.3	10.2
$C_7H_7Br_4N_4O_{0.5}Zn$				15.6	1.3	10.4
$[(L^\#)ZnI_2]$	**20**	310dec	75	13.8	1.0	8.5
$C_7H_6Br_2I_2N_4Zn$				13.4	1.0	9.0
$[(L^\#)_2Zn(CF_3SO_3)_2] \cdot 2H_2O$	**21**	293dec	98	19.9	1.6	10.9
$C_{16}H_{16}Br_4F_6N_8O_8S_2Zn$				19.0	1.6	11.1
$[(L^\#)_2Zn(ClO_4)_2] \cdot 2H_2O^a$	**22**	310dec	87	19.1	1.6	11.9
$C_{14}H_{16}Br_4Cl_2N_8O_{10}Zn$				18.4	1.8	12.3
$[(L^\#)Zn(NO_3)_2] \cdot H_2O$	**23**	256dec	62	16.8	1.4	16.3
$C_7H_8Br_2N_6O_7Zn$				16.4	1.6	16.4
$[(L^\#)_3Zn(BF_4)_2]$	**24**	350dec	56	22.2	1.6	13.9
$C_{21}H_{18}B_2Br_6F_8N_{12}Zn$				21.8	1.6	14.5
$[(L^\#)CdCl_2]$	**25**	300dec	56	17.3	1.3	11.1
$C_7H_6Br_2CdCl_2N_4$				17.2	1.2	11.4
$[(L^\#)CdBr_2] \cdot EtOH$	**26**	250dec	76	17.0	1.4	9.4
$C_9H_{12}Br_4CdN_4O$				17.3	1.9	9.0
$[(L^\#)CdI_2] \cdot EtOH$	**27**	174–175	75	15.2	1.8	8.0
$C_9H_{12}Br_2CdI_2N_4O$				15.0	1.7	7.8
$[(L^\#)_2Cd(ClO_4)_2] \cdot 2H_2O^a$	**28**	304–305	96	18.1	1.9	11.3
$C_{14}H_{18}Br_4CdCl_2N_8O_{10}$				17.5	1.7	11.7
$[(L^\#)_2Cd(BF_4)_2] \cdot 2H_2O$	**29**	350dec	91	18.3	1.8	11.8
$C_{14}H_{16}B_2CdBr_4F_8N_8O_2$				18.0	1.7	12.0

Table 1. *Continued*

Compound	No	M.p. (°C)	Yield (%)	Elem. An. (found %)[b] C	H	N
$[(L^{\#})Cd(NO_3)_2] \cdot H_2O$	**30**	282–283	86	15.3	1.3	15.2
$C_7H_8Br_2CdN_6O_7$				15.0	1.4	15.0
$[(L^{\#})HgCl_2]$	**31**	245–247	56	14.8	1.0	9.5
$C_7H_6Br_2Cl_2HgN_4$				14.6	1.0	9.7
$[(L^{\#})HgBr_2] \cdot EtOH$	**32**	204–207	55	15.4	1.6	7.3
$C_9H_{12}Br_4HgN_4O$				15.2	1.7	7.9
$[(L^{\circ})ZnCl_2] \cdot 1/2C_6H_{14}$	**33**	238–245	45	27.8	3.2	14.3
$C_{10}H_{13}Cl_4N_4Zn$				28.1	3.4	14.6
$[(L^{\circ})CdI_2]$	**34**	129–135	45	14.7	1.1	9.2
$C_7H_6Cl_2HgI_2N_4$				14.4	1.0	9.6
$[(L^{\circ})_2Cd(BF_4)_2]$	**35**	250dec	40	25.7	1.9	16.9
$C_{14}H_{12}B_2CdCl_4F_8N_8$				25.9	1.9	17.3
$[(L^{\circ})HgBr_2] \cdot 1/3C_6H_{14}$	**36**	158–165	63	17.4	2.0	8.8
$C_9H_{10.7}Br_2Cl_2HgN_4$				17.8	1.8	9.2

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

[b] Calculated values in the lower line.

ν(M–halide) absorptions at *ca* 330 and 290 cm^{-1} (Hg–Cl), 250–240 cm^{-1} (Cd–Cl), 230–200 cm^{-1} (Cd–Br and Hg–Br). Differently from that previously observed, the mercury(II) derivatives show separation of symmetric and antisymmetric stretching bands [18–25]. The Cd-chloride stretching frequencies are shifted to lower frequencies with respect to those found in [bis(4-methylpyrazol-1-yl)methane $CdCl_2$] [24]. The absorptions observed in the far-IR region are similar to those indicated for chlorine-bridged metal(II) dimers [27]. This fact together with the insolubility of the sample, agrees with our hypothesis that an oligomeric structure through bridging chloride groups is likely for compounds **9** and **25**.

The trifluoroacetato derivative **4** is a covalent molecule where the carboxylato ligand is monodentate. The $\Delta[\nu_a(CO_2^-)-\nu_s(CO_2^-)]$ values are of the same order of magnitude as the values reported for the complex (triphenylphosphine)gold(I) trifluoroacetate containing a monodentate $[CF_3COO]^-$ unity [28].

As previously observed in other analogous complexes [18–25], the perchlorato groups (adducts **6**, **12**, **17**, **22** and **28**) were found to be ionic; a single broad absorption at 1100 cm^{-1} being observed [29].

The tetrafluoroborate derivatives **7**, **13**, **24**, **29** and **38** exhibit in the region 1100–950 cm^{-1} a more complex pattern with respect to analogous derivatives with other poly(pyrazol-1-yl)alkanes. It has been previously noted that polymeric or oligomeric structures linked by bridging BF_4^- groups in some cases containing ionic tetrahedral BF_4^- unities, are often possible for this kind of derivatives [11,18–25].

The IR spectra of derivatives **8**, **11**, **23** and **30** show bands typical of bidentate nitrato groups: the separation of the two highest frequency bands is higher than that observed in derivatives containing unidentate NO_3 [30,31]. In the far IR spectra these adducts show also broad absorption at *ca* 470 and 430 cm^{-1} due to M–O stretching vibrations. In derivatives **5**, **6**, **11**, **13**, **19**, **21**–**23** and **28**–**30** we found broad absorption at *ca* 3400–3000 (antisymmetric and symmetric OH stretchings) and at 1640–1600 cm^{-1} (HOH bending). Also on the basis of previous reports [32] we propose these molecules as water trapped in the crystalline lattice, either by weak hydrogen bonds to the anion or to the halide of bis(pyrazol-1-yl)alkane ligand or by weak ionic bonds to the metal, or by both.

NMR spectra

^1H *NMR*. In the ^1H NMR spectra recorded for all the complexes in $CDCl_3$ or acetone, all the signals are displaced towards lower field upon coordination, as already seen in the zinc, cadmium or mercury derivatives of similar N_2-donor ligands [18–25]. The observed downfield shift is additional evidence in favour of the existence of the complexes in these solvents. The shift generally decreases with decreasing of the concentration of the samples. We also observed that 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 or 3 : 1 complexes than in the 1 : 1 adducts. In DMSO the displacement of the proton signals on going from the free ligand to the ligand in the adduct is negligible, in accordance with an extensive solvation and complete ligand dissociation in strongly coordinating solvents.

^{13}C *and* ^{113}Cd *NMR*. In the ^{13}C NMR spectra of sufficiently soluble derivatives we found a trend analogous to that observed in other bis(pyrazol-1-yl)methane adducts [19–25]. The bridging methylenes are shifted highfield upon complexation, whereas a negligible shift was observed for the methyl groups of L* adducts. The pyrazole-ring carbons are indeed dis-

Table 2. Selected IR data of compounds **1**–**36**[a]

Compound		>3000	1600–1500	<600	Other data
L*		3016w	1563m	539m, 521m, 495m, 465w, 368m, 296w, 257w, 228m	
$[(L^*)ZnCl_2]$	**1**	3016w	1556m	599m, 552m, 545m, 513w, 474w, 393w, 269m, 229m, 200m	ν(Zn–Cl) : 348s br, 320s
$[(L^*)ZnBr_2]$	**2**	3010w	1550m	598m, 551m, 544m, 511w, 474w, 391w, 334m, 308w, 199m	ν(Zn–Br) : 263s, 225s
$[(L^*)ZnI_2]$	**3**		1556m	600m, 549m, 510w, 471w, 391m, 339m, 316w, 277m, 267m	ν(Zn–I) : 221s, 190s
$[(L^*)Zn(CF_3COO)_2]$	**4**	3045w	1561m	600m, 545m, 522m, 508w, 399m, 354m 312w, 278m, 247w, 197m	ν(Zn–O) : 473s, 444m ν(C=O) : 1712br, 1673m, 1635m
$[(L^*)_3\{Zn(CF_3SO_3)_2\}_2 \cdot 3H_2O$	**5**		1562s	577m, 541m, 519m, 494w, 463m, 395m, 349s, 315m, 281m 258m, 228m	ν(O–H) : 3300br δ(O–H) : 1655br
$[(L^*)_2Zn(ClO_4)_2] \cdot 3H_2O$	**6**		1557m	599m, 558w, 544w, 522w, 509w, 489w, 473m, 465m, 392m 367w, 335m, 313w, 290m, 258w	$\nu(ClO_4)$: 1142s, 1107s, 1035s
$[(L^*)_2Zn(BF_4)_2]$	**7**		1563m	599m, 541m, 521m, 506m, 492w, 465m, 388w, 349br, 319w 275w, 258m, 225m	$\nu(BF_4)$: 1082s br
$[(L^*)Zn(NO_3)_2]$	**8**	3029w	1556s	600m, 552m, 548m, 514w, 474w, 394w, 341m, 327m, 277m	$\nu(NO_3)$: 1500s, 1280br ν(Zn–O) : 299s, 290s
$[(L^*)CdCl_2]$	**9**	3179w	1560m	600m, 539m, 521m, 495w, 466w, 419w, 397vw, 369w 351w, 279m, 230m	ν(Cd–Cl) : 254m, 246m
$[(L^*)CdBr_2]$	**10**		1551m	599sh, 545m, 509w, 470w, 397w, 347w, 277w, 267w, 192m	ν(Cd–Br) : 235m, 211m
$[(L^*)_3\{Cd(NO_3)_2\}_2] \cdot 2H_2O$	**11**	3040w	1558m	600m, 542m, 507m, 471m, 403m, 358m, 351m 311w, 278m, 238m, 202m	ν(O–H) : 3300br ; δ(O–H) : 1636m $\nu(NO_3)$: 1500s, 1280br
$[(L^*)_2Cd(ClO_4)_2]$	**12**	3171w, 3053w	1558m	600sh, 544m, 508m, 472w, 403w, 359m, 323w, 279m, 244m	$\nu(ClO_4)$: 1145s, 1133s, 1119s, 1037s
$[(L^*)_2Cd(BF_4)_2] \cdot 2H_2O$	**13**	3051w	1561m	600m, 545w, 540w, 507w, 472w, 398br, 352m, 279m 247w, 232w, 224w	$\nu(BF_4)$: 1100–1000br ν(O–H) : 3400br ; δ(O–H) : 1650br
$[(L^*)HgCl_2]$	**14**		1556m	600m, 546m, 534w, 496m, 468w, 374w, 308w, 269w, 232m	ν(Hg–Cl) : 337s, 292m
$[(L^*)HgBr_2]$	**15**		1556m	600s, 541s, 504m, 467m, 395m, 346m, 309w, 272m	ν(Hg–Br) : 233s, 202s
$[(L^*)HgI_2]$	**16**		1560w	598m, 538m, 501w, 465w, 391m, 342m, 305m, 270m, 228m, 206m	
$[(L^*)_2Hg(ClO_4)_2]$	**17**	3041w	1557m	604m, 553w, 539w, 511w, 471w, 398w, 356m, 348m, 283m 273m, 245m, 227w	$\nu(ClO_4)$: 1129s, 1101s, 1044s
$L^\#$		3136m, 3120m 3099m, 3011m	1525m	605s, 444m, 414m, 398w, 353w, 280w, 247w, 225w	
$[(L^\#)ZnCl_2]$	**18**	3129m, 3119m 3020m, 3009m	1527m 1507w	600m, 474m, 406m, 268w, 197m	ν(Zn–Cl) : 344s, 317s
$[(L^\#)ZnBr_2] \cdot 1/2H_2O$	**19**	3122m, 3000m	1526m	599m, 593m, 473m, 406m, 334w, 304w	ν(Zn–Br) : 265s, 229s ν(O–H) : 3500br ; δ(O–H) : 1640br

[a] Nujol mull.

Table 2. *Continued*

Compound		>3000	1600–1500	<600	Other data
$[(L^{\#})ZnI_2]$	**20**	3119m, 3000m	1526w 1509w	599m, 592m, 472m, 408m, 304m	ν(Zn–I) : 225m, 210m, 195m
$[(L^{\#})_2Zn(CF_3SO_3)_2]\cdot 2H_2O$	**21**	3136m, 3047m	1533m 1507m	600m, 577m, 519m, 471m, 411m, 383w, 351w, 311m, 270w 201m	$\nu(SO_3)$: 1270br ; ν(C–F) : 1033s ν(O–H) : 3400br ; δ(O–H) : 1670br
$[(L^{\#})_2Zn(ClO_4)_2]\cdot 2H_2O$	**22**	3133m, 3120m 3047m, 3000sh	1533w 1507w	600m, 472w, 407m, 352w, 326w, 280w, 247w, 225w	$\nu(ClO_4)$: 1110s br ν(O–H) : 3400br ; δ(O–H) : 1640br
$[(L^{\#})Zn(NO_3)_2]\cdot H_2O$	**23**	3166w, 3114w	1530sh	600m, 411m, 383w, 376w, 358w, 305m, 263w, 255w, 245w	ν(Zn–O) : 472m $\nu(NO_3)$: 1500s br, 1280br ν(O–H) : 3400br ; δ(O–H) : 1650br
$[(L^{\#})_3Zn(BF_4)_2]$	**24**	3132m, 3040w	1528m	600m, 526w, 516w, 470m, 404m, 381w, 360w, 296w, 225m	$\nu(BF_4)$: 1080s br
$[(L^{\#})CdCl_2]$	**25**	3134w, 3023w	1530m	597m, 441w, 424m, 356w, 297w, 281w	ν(Cd–Cl) : 262m
$[(L^{\#})CdBr_2]\cdot EtOH$	**26**	3115m, 3011w	1525w	598m, 461m, 400m, 290m, 255w, 243w	ν(Cd–Br) : 222w, 211sh
$[(L^{\#})CdI_2]\cdot EtOH$	**27**	3123w	1516m	598m, 519w, 458m, 419w, 398m, 369w, 352w, 325w, 302w	ν(O–H) : 3400br ; δ(O–H) : 1650br
$[(L^{\#})_2Cd(ClO_4)_2]\cdot 2H_2O$	**28**	3113w	1529m	599m, 463w, 425w, 403w, 387w, 291w, 241w, 231w, 216w	$\nu(ClO_4)$: 1080s br ν(O–H) : 3420br ; δ(O–H) : 1630br
$[(L^{\#})_2Cd(BF_4)_2]\cdot 2H_2O$	**29**	3128w, 3046w	1557m	600m, 523w, 465m, 427w, 348w, 297w, 279w, 259w	$\nu(BF_4)$: 1100s br ν(O–H) : 3500br ; δ(O–H) : 1650br
$[(L^{\#})Cd(NO_3)_2]\cdot H_2O$	**30**	3124w	1526sh	598m, 415m, 372w, 300w, 269w, 245w, 220w, 210w	ν(Cd–O) : 465m $\nu(NO_3)$: 1500s br, 1300br ν(O–H) : 3500br ; δ(O–H) : 1650br
$[(L^{\#})HgCl_2]$	**31**	3176w, 3134w 3120w	1557w 1522w	605s, 439w, 422m, 242w, 227w	ν(Hg–Cl) : 342s
$[(L^{\#})HgBr_2]\cdot EtOH$	**32**	3161w, 3126w 3115w	1520sh	600m, 437w, 419m, 349w, 326w, 3032w, 212w	ν(Hg–Br) : 247m
L°		3110w, 3050w	1556w	598m, 465w, 424w	
$[(L^{\circ})ZnCl_2]\cdot 1/2C_6H_{14}$	**33**	3110m, 3046w	1538w	597m, 528m, 471m, 428m, 389w, 350w, 277br sh, 231w	ν(Zn–Cl) : 318s, 293s
$[L^{\circ})CdI_2]$	**34**	3168w, 3103w	1559w	598m, 463m, 412m, 279w, 266w, 256w, 227w, 208m, 201m	
$[(L^{\circ})_2Cd(BF_4)_2]$	**35**	3168w, 3107w		600br, 475m, 425m, 282m	$\nu(BF_4)$: 1140s br
$[(L^{\circ})HgBr_2]\cdot C_6H_{14}$	**36**	3133w, 3120w	1558w 1532w	600m, 504w, 465w, 424m, 399w, 344w, 323w, 279w	ν(Hg–Br) : 247m

[a] Nujol mull.

Table 3. Conductivity data and molecular weight determinations of selected bis(pyrazol-1-yl)alkane derivatives

		Molecular weight determinations[a]				Conductivity data[b]		
Compound	No	F.W.	M.W.	r	conc.	Λ	solv.	conc
$[(L^*)ZnCl_2]$	**1**	409.4	273	0.67	0.11	5.2	acetone	0.97
			366	0.89	0.21			
$[(L^*)ZnBr_2]$	**2**	498.3				1.3	acetone	0.95
$[(L^*)ZnI_2]$	**3**	592.4				1.8	acetone	1.00
						0.2	CH_2Cl_2	1.07
$[(L^*)Zn(CF_3COO)_2]$	**4**	564.6	285	0.50	0.10	4.9	acetone	0.89
			333	0.59	0.16	0.2	CH_2Cl_2	0.96
$[(L^*)_3\{Zn(CF_3SO_3)_2\}_2]\cdot 3H_2O$	**5**	1600.6				169.7	acetone	0.99
$[(L^*)_2Zn(ClO_4)_2]\cdot 3H_2O$	**6**	864.7	304	0.35	0.09	180.3	acetone	1.17
$[(L^*)_2Zn(BF_4)_2]$	**7**	785.3				81.7	acetone	0.98
$[(L^*)Zn(NO_3)_2]$	**8**	462.6	246	0.53	0.05	7.1	acetone	1.00
			290	0.63	0.12	1.2	CH_2Cl_2	1.00
$[(L^*)CdCl_2]$	**9**	456.5				16.4	acetone	0.44
$[(L^*)CdBr_2]$	**10**	545.4				6.5	acetone	1.00
$[(L^*)_3\{Cd(NO_3)_2\}_2]\cdot 2H_2O$	**11**	1328.4	443	0.33	0.24	29.1	acetone	0.87
			587	0.44	0.74			
$[(L^*)_2Cd(ClO_4)_2]$	**12**	857.6	303	0.35	0.08	159.4	acetone	1.01
$[(L^*)_2Cd(BF_4)_2]\cdot 2H_2O$	**13**	868.4				166.0	acetone	1.00
$[(L^*)HgCl_2]$	**14**	544.7	331	0.61	0.09	7.9	acetone	0.99
			359	0.66	0.20			
			440	0.81	0.47			
$[(L^*)HgBr_2]$	**15**	633.6	316	0.50	0.11	7.6	acetone	1.01
			322	0.51	0.25			
$[(L^*)HgI_2]$	**16**	727.6	245	0.34	0.10	0.8	acetone	0.99
			294	0.40	0.18			
$[(L^*)_2Hg(ClO_4)_2]$	**17**	945.8				242.0	acetone	1.01
$[(L^{\#})ZnCl_2]$	**18**	442.2				11.2	acetone	1.02
$[(L^{\#})ZnBr_2]\cdot 1/2H_2O$	**19**	540.1				5.6	acetone	1.01
$[(L^{\#})ZnI_2]$	**20**	625.1				3.0	acetone	1.01
$[(L^{\#})_2Zn(CF_3SO_3)_2]\cdot 2H_2O$	**21**	1011.5				119.6	acetone	0.98
$[(L^{\#})_2Zn(ClO_4)_2]\cdot 2H_2O$	**22**	912.2				175.2	acetone	1.09
$[(L^{\#})Zn(NO_3)_2]\cdot H_2O$	**23**	513.4				11.9	acetone	1.06
$[(L^{\#})_3Zn(BF_4)_2]$	**24**	1156.9				119.7	acetone	0.98
$[(L^{\#})CdCl_2]$	**25**	480.3					Insoluble	
$[(L^{\#})CdBr_2]\cdot EtOH$	**26**	624.2				17.3	acetone	0.92
$[(L^{\#})CdI_2]\cdot EtOH$	**27**	718.2				27.1	acetone	0.55
$[(L^{\#})_2Cd(ClO_4)_2]\cdot 2H_2O$	**28**	959.3				165.5	acetone	0.93
$[(L^{\#})_2Cd(BF_4)_2]\cdot 2H_2O$	**29**	933.3				169.2	acetone	0.91
$[(L^{\#})Cd(NO_3)_2]\cdot H_2O$	**30**	560.4				9.0	acetone	1.07
$[(L^{\#})HgCl_2]$	**31**	577.5	292	0.51	0.09	0.4	acetone	1.30
$[(L^{\#})HgBr_2]\cdot EtOH$	**32**	712.4				2.3	acetone	0.08
$[(L^{\circ})ZnCl_2]\cdot 1/2C_6H_{14}$	**33**	380.4	212	0.55	0.04	27.3	acetone	1.31
$[(L^{\circ})CdI_2]$	**34**	583.3				19.7	acetone	1.12
$[(L^{\circ})_2Cd(BF_4)_2]$	**35**	649.2				6.4	acetone	0.42
$[(L^{\circ})HgBr_2]\cdot 1/3C_6H_{14}$	**36**	606.2				62.7	acetone	1.06

[a] Conc. is %.w/w, r = M.W./F.W.

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

placed downfield, as required by electron density transfer from the ring to the metal upon coordination. This is a big difference between bis(pyrazol-1-yl)methane-type ligands and 2,2′-bipyridine or ortho-phenanthroline [33], the lack of transmission of electronic effects from one pyrazole to the other because of the insulating property of the bridging methylene groups.

The ^{113}Cd NMR spectrum was measured only for the derivative **11** which is the only Cd(II) derivative sufficiently soluble in $CDCl_3$ solution. The ^{113}Cd resonance observed (+29.4 ppm) was with natural abundance Cd in solutions with concentration in the range 0.5–1.0 × 10^{-3} in $CDCl_3$. The resonance was deshielded relative to 0.1 M $Cd(ClO_4)_2$ solution reference. On the basis of solution data, as well as of previous literature reports [34–38], one might be tempted to assign to Cd center in **11** higher coordination number than six. However it has been previously observed

Table 4. ^1H NMR data of compounds **1**–**36**[a]

Compound		Solvent	CH_2	3 or 5 CH_3	3 or 5-H	Other data
L^*		$CDCl_3$	6.03	2.18, 2.40		
		acetone	6.16	2.09, 2.44		
$[(L^*)ZnCl_2]$	**1**	$CDCl_3$	6.40	2.45, 2.48		
$[(L^*)ZnBr_2]$	**2**	$CDCl_3$	6.42	2.44, 2.53		
$[(L^*)ZnI_2]$	**3**	$CDCl_3$	6.43	2.46, 2.58		
$[(L^*)Zn(CF_3COO)_2]$	**4**	$CDCl_3$	6.49	2.33, 2.45		
$[(L^*)_3\{Zn(CF_3SO_3)_2\}_2]\cdot 3H_2O$	**5**	acetone	6.48	1.89, 2.46		3.7br (H_2O)
$[(L^*)_2Zn(ClO_4)_2]\cdot 3H_2O$	**6**	acetone	6.54	1.97, 2.49		2.8br (H_2O)
$[(L^*)_2Zn(BF_4)_2]$	**7**	$CDCl_3$	6.04br	2.10, 2.43		
		acetone	6.30	2.15, 2.52		
$[(L^*)Zn(NO_3)_2]$	**8**	$CDCl_3$	6.27	2.33, 2.47		
$[(L^*)CdCl_2]$	**9**	$CDCl_3$	6.05	2.18, 2.40		
		acetone	6.42	2.22, 2.50		
$[(L^*)CdBr_2]$	**10**	acetone	6.65	2.36, 2.59		
$[(L^*)_3\{Cd(NO_3)_2\}_2]\cdot 2H_2O$	**11**	$CDCl_3$	6.27	2.24, 2.43		2.8br (H_2O)
$[(L^*)_2Cd(ClO_4)_2]$	**12**	acetone	6.60	2.15, 2.56		
$[(L^*)_2Cd(BF_4)_2]\cdot 2H_2O$	**13**	acetone	6.65	2.11, 2.59		3.1br (H_2O)
$[(L^*)HgCl_2]$	**14**	$CDCl_3$	6.30	2.31, 2.39		
$[(L^*)HgBr_2]$	**15**	$CDCl_3$	6.29	2.31, 2.38		
$[(L^*)HgI_2]$	**16**	$CDCl_3$	6.14	2.23, 2.39		
$[(L^*)_2Hg(ClO_4)_2]$	**17**	acetone	6.99	2.69, 2.86		
$L^{\#}$		$CDCl_3$	6.20		7.50, 7.65	
		acetone	6.40		7.54, 8.07	
		DMSO	6.30		7.65, 8.23	
$[(L^{\#})ZnCl_2]$	**18**	acetone	6.76		7.86, 8.31	
$[(L^{\#})ZnBr_2]\cdot 1/2H_2O$	**19**	acetone	6.88		7.95, 8.35	4.21, 4.23 (H_2O)
$[(L^{\#})ZnI_2]$	**20**	acetone	6.95		8.03, 8.50	
$[(L^{\#})_2Zn(CF_3SO_3)_2]\cdot 2H_2O$	**21**	acetone	6.79		7.92, 8.38	4.40br (H_2O)
$[(L^{\#})_2Zn(ClO_4)_2]\cdot 2H_2O$	**22**	acetone	6.70		8.00, 8.42	4.45br (H_2O)
$[(L^{\#})Zn(NO_3)_2]\cdot H_2O$	**23**	acetone	6.70		7.93, 8.38	4.40br (H_2O)
$[(L^{\#})_3Zn(BF_4)_2]$	**24**	acetone	6.70		7.74, 8.25	
$[(L^{\#})CdCl_2]$	**25**	acetone	6.40		7.67, 8.25	
$[(L^{\#})CdBr_2]\cdot EtOH$	**26**	acetone	6.65		7.70, 8.25	1.40t, 3.40br (EtOH)
$[(L^{\#})CdI_2]\cdot EtOH$	**27**	acetone	6.45		7.55, 8.10	1.40t, 3.40q (EtOH)
$[(L^{\#})_2Cd(ClO_4)_2]\cdot 2H_2O$	**28**	acetone	6.80		7.90, 8.40	3.84 (H_2O)
$[(L^{\#})_2Cd(BF_4)_2]\cdot 2H_2O$	**29**	acetone	6.80		7.95, 8.43	4.30br (H_2O)
$[(L^{\#})Cd(NO_3)_2]\cdot H_2O$	**30**	acetone	6.60		7.70, 8.20	2.90br (H_2O)
$[(L^{\#})HgCl_2]$	**31**	acetone	6.43		7.56, 8.08	
		$CDCl_3$	6.22		7.52, 7.70	
$[(L^{\#})HgBr_2]\cdot EtOH$	**32**	acetone	6.46		7.58, 8.09	1.40t, 3.40q (EtOH)
L°		acetone	6.26		7.40, 7.96	
$[(L^{\circ})ZnCl_2]\cdot 1/2C_6H_{14}$	**33**	acetone	6.52		7.65, 8.11	
$[(L^{\circ})CdI_2]$	**34**	acetone	6.72		7.80, 8.22	
$[(L^{\circ})_2Cd(BF_4)_2]$	**35**	acetone	6.40		7.55, 8.06	
$[(L^{\circ})HgBr_2]\cdot 1/3C_6H_{14}$	**36**	$CDCl_3$	6.19		7.50, 7.64	1.05t, 1.50q, 1.68m

[a] δ in ppm from internal TMS.

that the ^{113}Cd chemical shift may be positive or negative and not necessarily depends upon coordination number or Cd–O distance, but rather upon the number of ligand lone pair electrons and basicity of the donor [35,37]. The value observed for **11** is in the range reported for hexacoordinate cadmium(II) complexes containing six oxygen-donor ligands or compounds in which one or two nitrogen atoms are bound to Cd and the remaining coordination positions are occupied by oxygen-donor ligands [34–38]. This data agrees with the dissociation (4) proposed for **11** in $CHCl_3$ solution.

CONCLUSIONS

The combined evidence from measurements carried out in solid state and in solution (IR, molecular weight determinations, conductivity, proton and carbon NMR spectra) gives here a picture which is different from that obtained when other chelating ligands were considered.

The bis(4-halopyrazol-1-yl)alkanes seem to be very modest donors: in the derivatives here described the ligand/metal ratio, frequently a measure of the donat-

Table 5. ^{13}C NMR data of selected bis(halopyrazol-1-yl)alkane compounds

Compound	Solvent	CH_2	CH_3	C(3)	C(5)	C(4)
L*	acetone	62.3	9.9, 11.7	146.2	137.9	109.2
1	acetone	59.0	9.9, 11.7	150.1	141.4	111.0
4	$CDCl_3$	57.0	9.4, 11.8	148.4	139.1	109.0
8	$CDCl_3$	58.1	9.4, 10.8	150.6	142.0	110.2
12	acetone	59.3	8.7, 10.5	n.o[a]	n.o	n.o
L$^{\#}$	acetone	66.8		142.2	131.8	94.9
19	acetone	65.5		143.1	133.6	95.5
20	acetone	64.6		143.7	134.8	95.6
21	acetone	64.3		143.8	135.1	95.5
22[b]	acetone	64.3		144.2	134.8	95.4
23	acetone	63.1		143.0	133.7	94.3
24	acetone	65.0		143.8	134.4	95.5
25	acetone	64.7		141.6	131.6	95.2

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

[b] 121.9q (CF_3), J(C–F): 318.4 Hz.

ing ability, is higher than 1 only with good acceptors such as $M(ClO_4)_2$ and $Cd(BF_4)_2$ and the ratio is 3 only in derivative **24**. In addition, the bis(4-halopyrazol-1-yl)alkanes, differently from bis(4-methylpyrazol-1-yl)methane and bis(3,5-dimethylpyrazol-1-yl)methane, are not able to displace the nitrato ligand from the coordination sphere of the metal center also if the reactions were carried out under forcing conditions, i.e. strong excess of the donor and refluxing solvent. The molecular weight determinations indicated that the bis(4-halopyrazol-1-yl)alkane complexes are almost dissociated in chloroform solution, whereas the derivatives of bis(4-methylpyrazol-1-yl)methane, bis(3,5-dimethylpyrazol-1-yl)methane and bis(pyrazol-1-yl)methane, in $CHCl_3$ at the same temperature and concentration, showed values of *r* (ratio between the osmometric and calculated molecular weight) close to the unity.

Significant difference in behaviour was observed also between L*, L$^{\#}$ and L$^{\circ}$; the donating ability can be easily correlated to basicity and steric hindrance of the heterocyclic ring: L* which is more basic than L$^{\circ}$ and L$^{\#}$, is also the best donor ligand, but the steric hindrance due to the two methyl groups near to the coordination site, may explain why no 3 : 1 adduct of L* are obtained.

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