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Cobalt(II) and Nickel(II) Coordination Compounds Derived from 3,3′, 5,5′-Tetramethyl-4,4′-bi-1H-pyrazole, 3,3′, 5,5′-Tetramethyl-4,4′ Methylene-bis-1H-Pyrazole and 4,4′-Methylene-bis-1H-Pyrazole

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The bidentate ligands 3,3′,5,5′-tetramethyl-4,4′-bi-1H-pyrazole (tmbpz) 3,3′,5,5′-tetramethyl-4,4′-methylene-bis-1H-pyrazole (tmmbpz) and 4,4′ methylene-bis-1H-pyrazole (mbpz) react with cobalt(II) and nickel(II) chlorides to give complexes with the formula $MCl_2(LL)$ *(M = Co, LL = tmmbpz; tmmbpz; M = Ni, LL = tmmbzp or* $MCl_2(LL)_2$ *(M = Co, LL = mbpz; M = Ni, LL = tmbpz, tmmbpz, mbpz). Similarly the reactions of tmbpz and tmmbpz with cobalt(II) and nickel(II) nitrates give complexes of formula* $M(NO_3)_2(LL)$ *(M = Co, LL = tmmbpz) or* $M(NO_3)_2(LL)_2$ *(M = Co, Ni; LL = tmbpz, tmmbpz). The reaction products are generally independent of the molar ratio (M:LL) of reactants, except in the reactions of tmmbpz with nickel(II) chloride and cobalt(II) nitrate.*

The $CoX_2(LL)$ *complexes are pseudotetrahedral species, whereas* $NiCl_2(tmmbpz)$ *seems to contain five-coordinate dimeric units bonded through two bridging chloro ligands. The* $MX_2(LL)_2$ *complexes are pseudo-octahedral species; some of them are clearly tetragonally distorted, particularly the chlorides.*

Dimeric or polymeric structures were proposed for the complexes with bridging bipyrazole molecules, as a consequence of the bidentate, non-chelating nature of the ligands.

Introduction

Pyrazole chemistry was extensively investigated a long time ago. However the coordination chemistry of the substituted pyrazole ligands is relatively recent [1, 2]. Up to date only coordination compounds of a bidentate bipyrazole, bis(3,5-dimethylpyrazolyl)methane with Co(II) and Ni(II) have been described [3]. This molecule consists of two pyrazole rings bonded to a methylene group through the N-atoms and acts as a chelating ligand, giving complexes of composition $MX_2(LL)$ and $MX_2(LL)_2$. The structure determination of the complex of the first type, $NiCl_2(LL)$, has demonstrated the dimeric nature of this complex, in which each five-coordinate Ni^{2+} ion is surrounded by one bipyrazole ligand, one terminal chloro ligand and two bridging chloro ligands [4].

This work describes the preparation and properties of Co(II) and Ni(II) complexes with ligands containing two pyrazole rings: 3,3′, 5,5′-tetramethyl-4, 4′-bipyrazole (tmbpz), 3,3′,5,5′-tetramethyl-4,4′-methylene-bis-1H-pyrazole (tmmbpz) and 4,4′-methylene-bipyrazolyl (mbpz). These molecules can act as bidentate bridging ligands through the pyridine-type nitrogen atoms. The prototropy present in these bipyrazole molecules renders the N(1), N(2) and N(1′), N(2′) positions of the ligands indistinguishable.

Polynuclear complexes of Rhodium(I) with tmbpz and tmmbpz have been recently reported [5]. On the other hand complexes of a similar bidentate non-chelating ligand, 4,4′-bi-1,2,4-triazole, with transition metal(II) thiocyanates have been described [6], for which double bridged polymeric structures have been proposed, the metal atom being tetragonally surrounded by nitrogen atoms from four equatorial bitriazole bridging molecules and two axial thiocyanate groups.

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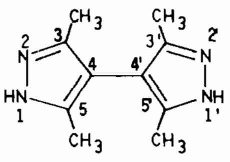
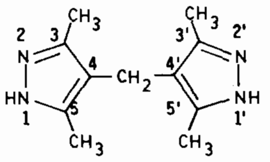
TABLE I. Analtyical Data and Physical Properties for Cobalt(II) and Nickel(II) Bipyrazole Complexes.

Compound	Colour	M.p. or dec. temp. (℃)	Analyses, found (calcd.) %				Magnetic data		Principal i.r. frequencies		
			C	H	N	Cl	μ_{eff} (B.M.)	θ (K)	ν(M–Cl)	ν(M–N)	ν(M–O)
$CoCl_2(tmbpz)\cdot \frac{1}{2}H_2O$	dark blue	>346	36.60 (36.49)	4.68 (4.59)	17.14 (17.03)	21.28 (21.56)	4.39(26 ℃)	−38	330s, 305s	230m	
$CoCl_2(tmmbpz)\cdot \frac{1}{2}H_2O$	dark blue	334[a]	38.39 (38.50)	4.99 (4.99)	16.85 (16.33)	21.11 (20.68)	4.35(27 ℃)	−35	330s, 310s	232s	
$CoCl_2(mbpz)_2$	pink-violet	318[a]	39.77 (39.45)	3.87 (3.75)	26.52 (26.30)	16.79 (16.64)	4.89(21 ℃)	−70	233vs, 222vs	212vs	
$Co(NO_3)_2(tmbpz)_2\cdot H_2O$	pink	230[a]	41.30 (41.31)	4.85 (5.16)	23.46 (24.09)		5.12(18 ℃)	−46		228s, 222s	245sh
$Co(NO_3)_2(tmmbpz)_2$	pink	240[a]	44.09 (44.67)	5.53 (5.41)	23.17 (23.69)		5.20(22 ℃)	−59		215sh, 205s	235sh
$Co(NO_3)_2(tmmbpz)\cdot H_2O$	purple	130–131	29.50 (32.60)	4.01 (4.48)	20.33 (20.74)		4.48(25 ℃)	−51		240m	266m
$NiCl_2(tmbpz)_2\cdot H_2O$	green	>346	44.44 (45.75)	5.45 (5.72)	21.43 (21.22)	13.43 (13.44)	3.24(27 ℃)	−35	246sh, 230s	217vs	
$NiCl_2(tmmbpz)_2$	green	310[a]	48.94 (49.10)	6.35 (5.95)	20.80 (20.83)	14.11 (13.18)	3.22(19 ℃)	−40	245sh, 228s	215vs, 210vs	
$NiCl_2(tmmbpz)$	yellow-orange	335[a]	39.84 (39.56)	5.08 (4.82)	16.69 (16.78)		3.20(28 ℃)	−17	280vs, 228s	273vs, 263vs	
$NiCl_2(mbpz)_2$	light blue	>346	39.83 (39.47)	3.87 (3.75)	26.50 (26.31)	15.96 (16.65)	3.08(19 ℃)	−31	246vs, 237vs	220vs	
$Ni(NO_3)_2(tmbpz)_2\cdot H_2O$	light blue	250[a]	41.67 (41.32)	4.79 (5.16)	23.95 (24.10)		3.23(24 ℃)	−50		245s	253sh
$Ni(NO_3)_2(tmmbpz)_2\cdot H_2O$	light blue	250[a]	43.43 (43.37)	5.44 (5.58)	22.81 (22.94)		3.27(25 ℃)	−30		225s, 222s	245sh

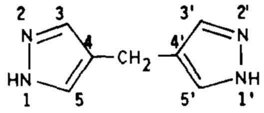
[a] It decomposes.



tmbpz



tmmbpz



mbpz

Pyrazole fits in the spectrochemical series in a place similar to that of pyridine or ammonia [7, 8]. On the other hand, the alkyl substituted pyrazoles show generally a stronger donor character than unsubstituted pyrazole [9, 10].

Results and Discussion

The reactions of the bidentate ligands tmbpz, tmmbpz and mbpz with the chlorides $MCl_2 \cdot 6H_2O$ (M = Co, Ni) in molar ratio 1:1 give complexes of composition $CoCl_2(tmbpz) \cdot \frac{1}{2}H_2O$, $NiCl_2(tmbpz)_2 \cdot H_2O$, $CoCl_2(tmmbpz) \cdot \frac{1}{2}H_2O$, $NiCl_2(tmmbpz)$, $CoCl_2(mbpz)_2$ and $NiCl_2(mbpz)_2$. Only one new complex of composition $NiCl_2(tmmbpz)_2$ was obtained from the reactions in molar ratios 1:2 and 1:3 (M:LL). The crystallization of $CoCl_2(tmmbpz) \cdot \frac{1}{2}H_2O$ in nitromethane/abs. ethanol yields a crystalline product of composition $CoCl_2(tmmbpz) \cdot 1/3EtOH$. The cobalt complexes of composition $CoCl_2(LL)$ are deep blue solids almost insoluble in organic solvents of medium polarity. However they could be recrystallized from absolute ethanol, yielding microcrystalline products. Nevertheless the crystallization from nitromethane/abs. ethanol yields a crystalline product suitable for structure determination. The remaining Co(II) and Ni(II) chlorocomplexes could not be recrystallized because of their insolubility. All these complexes react with water giving almost colourless solutions and are non-electrolytes, as was deduced from the molar conductance measurements in ethanol.

The reactions of tmbpz and tmmbpz with Cobalt(II) and Nickel(II) nitrates in molar ratio 1:1 give complexes of composition $M(NO_3)_2(tmbpz)_2 \cdot H_2O$ (M = Co, Ni), $Co(NO_3)_2(tmmbpz) \cdot H_2O$ and $Ni(NO_3)_2(tmmbpz)_2 \cdot H_2O$. Only one new complex, $Co(NO_3)_2(tmmbpz)_2$, was isolated from the reactions in molar ratio 1:2. The complexes of composition $M(NO_3)_2(LL)_2$ are soluble in water, ethanol and methanol, giving almost colourless solutions with molar conductance values corresponding to 1:2 electrolytes [11]. They are moderately soluble in nitrobenzene and acetone, giving non-conducting solutions. $Co(NO_3)_2(tmmbpz) \cdot H_2O$ is soluble in organic solvents of medium polarity without colour change and is a non-electrolyte in acetone.

The analytical data and physical properties of the complexes are given in Table I.

The reciprocal mol-susceptibility, $1/\chi'_M$ of all these complexes varies linearly with the temperature, and the θ values can be used as an indication of the quantity of the increasing of μ_{eff} with temperature.

The magnetic moment values (Table I) obtained for the $CoX_2(LL)$ complexes correspond to a high-spin tetrahedral coordination [3, 10, 12]. This coordination was confirmed by the electronic spectra (Table II). The ${}^4T_1(P) \leftarrow {}^4A_2$ transition (ν_3) shows the typical splitting, corresponding to a pseudotetrahedral configuration, in the chlorocomplexes only. The ${}^4T_1(F) \leftarrow {}^4A_2$ transition (ν_2) falls in the near i.r. and could not be observed with our apparatus. The pseudotetrahedral coordination of Co(II) has been proved by the structure determination of $CoCl_2(tmmbpz) \cdot 1/3EtOH$, which consists of dimeric $CoCl_2(\mu\text{-tmmbpz})_2CoCl_2$ units bonded through N–H···Cl, EtOH···Cl and N–H···OHEt hydrogen bonding [13]. Although the crystal structures of $CoCl_2(tmmbpz) \cdot \frac{1}{2}H_2O$, $CoCl_2(tmbpz) \cdot \frac{1}{2}H_2O$ and $Co(NO_3)_2(tmmbpz) \cdot H_2O$ could not be determined, we can suppose a similar structure with $X_2Co(\mu\text{-LL})_2CoX_2$ dimeric units for all these tetrahedral complexes. The splitting of the doubly degenerate $\nu(NO_2)$ mode of the nitrate group in the i.r. spectrum of $Co(NO_3)_2(tmmbpz) \cdot H_2O$ (1435, 1305 cm^{-1}) indicates clearly the monodentate coordination of both nitrate ligands in this complex.

In the $CoX_2(LL)_2$ complexes the splitting of the ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ band indicates clearly a tetragonal distortion of the octahedral symmetry and is similar with those found for $CoX_2(mpz)_4$ complexes (X = Cl, NO_3) [9]. These tetragonal Co(II) compounds all show the usual temperature dependence of the magnetic moment, as expected for six-coordinate Co^{2+} ions [14]. The monodentate coordination of the nitrate groups in the $Co(NO_3)_2(LL)_2$ compounds is clearly indicated by the splitting of the doubly degenerate $\nu(NO_2)$ stretching mode (1420–1440 cm^{-1}, 1310–1315 cm^{-1}) and the small separation between the combination bands at *ca.* 1750 cm^{-1} (1735, 1755 cm^{-1}) [15].

TABLE II. Reflectance Spectra ($cm^{-1} \times 10^{-3}$) of Cobalt(II) and Nickel(II) Bipyrazole Complexes.

Pseudotetrahedral Co(II) complexes		$^4T_1(P) \leftarrow {}^4A_2(F)$			Other bands
$CoCl_2$(tmbpz)·½H_2O		15.75vs; 17.39vs			19.05sh; 19.80sh; 21.74sh; 33.33s; 38.46s; 46.51w
$CoCl_2$(tmmbpz)·½H_2O		15.75vs; 17.54vs			21.05w; 22.99vw; 23.81w; 25.64w; 31.75s; 38.46s; 46.51w
$Co(NO_3)_2$(tmmbpz)·H_2O		18.52vs			21.28sh; 33.33s; 38.46s
Pseudooctahedral Co(II) complexes	$^2T_{1g}(G)$, $^2T_{2g}(G) \leftarrow {}^4T_{1g}(F)$		$^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	Other bands
$CoCl_2(mbpz)_2$	14.97sh		15.82w	18.42m; 19.80m	22.99w; 26.32sh
$Co(NO_3)_2(tmbpz)_2 \cdot H_2O$	15.38sh		22.53m	18.45s; 19.65s	33.11vs; 41.67vs
$Co(NO_3)_2(tmmbpz)_2$	15.38sh		23.26m	18.35s; 19.61s	31.74vs; 39.27vs
Pseudooctahedral Ni(II) complexes	$^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$	$^1E_g(D) \leftarrow {}^3A_{2g}(F)$	$^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$	$^3T_{2g}(P) \leftarrow {}^3A_{2g}(F)$	Other bands
$NiCl_2(tmbpz)_2 \cdot H_2O$		12.58sh	13.70s; 15.15s	24.51s	37.04sh; 42.02vs
$NiCl_2(mbpz)_2$	11.30m	13.70w	13.16m; 16.39s	26.32s	42.74vs
$NiCl_2(tmmbpz)_2$		12.50sh	14.43s	24.27s	32.26sh; 39.22s
$Ni(NO_3)_2(tmbpz)_2 \cdot H_2O$		13.39w	16.08s	26.39s	33.33sh; 41.67vs
$Ni(NO_3)_2(tmmbpz)_2 \cdot H_2O$		13.12w	15.27s	25.00s	31.25sh; 35.71sh; 40.00vs
Special cases		ligand-field transitions			Other bands
$NiCl_2$(tmmbpz)*		12.20sh; 12.90s; 19.05sh; 22.73m			28.57s; 30.77sh; 33.33sh 38.46vs

*Ni(II) is probably five-coordinated in this complex.

The complexes of formula $NiX_2(LL)_2$ show magnetic moments in the usual range for six-coordinate Ni^{2+} ions. The lowering of μ_{eff} with decreasing temperature may be an indication of a large zero-field splitting of the ground state [16]. This fact has also been observed in tetragonal $NiX_2(mpz)_4$ complexes [12]. Only the ligand-field spectra of $NiCl_2(tmbpz)_2 \cdot H_2O$ and $NiCl_2(mbpz)_2$ show a noticeable splitting of the $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ band, caused by the strong tetragonal distortion usually observed in the *trans*-$NiX_2(L)_4$ complexes (L = pyrazole, 5-methylpyrazole, X = Cl, Br), which increases in the order Br < Cl and has been attributed to strong $N-H \cdots X$ bonds between the pyrazole and the halide ligands [17, 18]. Most of the *trans*-$NiX_2(L)_4$ complexes (L = nitrogen donor ligand) show tetragonal splitting only in the $^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$ transition. The higher energy component of this split band is also observed in the ligand-field spectrum of $NiCl_2(mbpz)_2$. The forbidden $^1E_g(D) \leftarrow {}^3A_{2g}(F)$ transition appears in all these spectra as a weak band or as a shoulder in the range 12500–13700 cm^{-1}.

The μ_{eff} values of $NiCl_2(tmmbpz)$ fit in the range of the six-coordinate or high-spin five-coordinate complexes of Ni^{2+} and increase with the temperature. The electronic spectra, colour and magnetic moment at room temperature of this complex are very similar to those of the dimeric complex $Ni_2Cl_4(LL)_2$ (LL = bis(3,5-dimethylpyrazolyl)methane) mentioned above [4], which suggests a dimeric five-coordinate configuration for $NiCl_2(tmmbpz)$. This would imply the presence of terminal and bridging chloro ligands and a polymeric structure formed by dimeric pentacoordinated units.

The principal infrared bands of the complexes are listed in Table I. Coordinated and free ligands have somewhat different i.r. spectra, and the changes are almost independent of the metal ion. The most significant changes in the ligand bands are observed in the 550–700 cm^{-1} region, where new bands appear, and in the 3500–3000 cm^{-1} region, where the broad band, typical of the NH group with hydrogen bonding which exhibits three maxima in the free ligands becomes narrower and shifts towards the higher frequencies in the complexes, showing a more broad and structured shape in some hydrates. However, in general the complexes containing lattice water show no bands clearly assignable to the $\nu(OH)$ and $\delta(HOH)$ vibration modes of water, and there are very few differences between the spectra corresponding to similar compounds with and without lattice water. The spectra of $Co(NO_3)_2(tmmbpz)_2$ and $Ni(NO_3)_2(tmmbpz)_2 \cdot H_2O$ are indistinguishable in the 3500–300 cm^{-1} and 1650–1600 cm^{-1} regions. On the other hand the spectrum of $CoCl_2(tmmbpz) \cdot 1/3EtOH$ is very similar to that of the hydrate, the principal differences observed in the 3500–300 cm^{-1} region being due probably to a different structure of the hydrogen bond system. The presence of lattice water is clearly proved by thermogravimetric analysis.

The great similarity of the spectra of $MX_2(LL)_2$ complexes with the same anion and ligand, which show differences only in the $\nu(M-X)$ and $\nu(M-N)$ stretching frequencies in the 300–200 cm^{-1} region, is to be noted.

In the $CoCl_2(LL)_n$ (n = 1, 2) complexes the Co–Cl stretching frequencies fall in the range expected for terminal Co–Cl bonds in the respective tetrahedral or octahedral coordination [19], and are similar to those observed for pyrazole complexes of $CoCl_2$ of equivalent composition [3, 20]. A slight shift of the $\nu(Co-Cl)$ bands is the only difference observed in the low-frequency region of the spectrum of $CoCl_2(tmmbpz) \cdot 1/3EtOH$ with respect to that of $CoCl_2(tmmbpz) \cdot ½H_2O$. The Co–N stretching frequencies are similar to those observed for pyrazole complexes of $CoCl_2$ of the same composition [3, 20].

In the spectra of the $NiCl_2(LL)_2$ complexes $\nu(Ni-Cl)$ and $\nu(Ni-N)$ appear at frequency values higher than in the corresponding Co(II) complexes, following the Irving–Williams sequence. The spectrum of $NiCl_2(tmmbpz)$ differs considerably in the low-frequency region from those of the tetrahedral $CoCl_2(LL)$ complexes. Two strong bands at 273 and 263 cm^{-1} were assigned to $\nu(Ni-N)$ stretching frequencies. A strong band at 280 cm^{-1}, assigned to $\nu(Ni-Cl_t)$, and a band at 228 cm^{-1}, assigned to $\nu(Ni-Cl_{br})$, are noticeably coincident with those assigned by Reedijk *et al.* for the five-coordinate $Ni_2Cl_4(LL)_2$ complex mentioned above [3]. This makes a polymeric structure highly probable through the bridging bipyrazole ligands containing dimeric units formed by two five-coordinate Ni(II) species bonded through two bridging chloro ligands.

The spectra of the nitrate complexes show the bands characteristic of the monodentate coordination of the anion described above. In the low-frequency region the $M(NO_3)_2(LL)$ complexes show only one structured band sensible to metal with a maximum centred at 205–228 cm^{-1} in the Co(II) complexes, which has been assigned to a $\nu(M-N)$ stretching frequency. The shoulders observed at the higher energy side of this band have been assigned to $\nu(M-O)$ stretching vibrations with the nitrate groups. The i.r. spectrum of $Co(NO_3)_2(tmmbpz) \cdot H_2O$ differs considerably from those of the $Co(NO_3)_2(LL)_2$ complexes in the low frequency region and the $\nu(Co-N)$ and $\nu(Co-O)$ stretching frequencies have been assigned to bands appearing at frequency values higher than in the 1:2 complex.

The presence of lattice water in several of these complexes has been confirmed by thermogravimetric analysis. In all cases lattice water is lost at relatively low temperatures, 40–150 °C. A greater weight loss at approximately the same temperatures appearing in Table I (m.p. or dec. temp.) includes the decomposition of complexes. Sometimes this second weight loss corresponds to sublimation of the ligand, as occurs in the case of $NiCl_2(tmmbpz)_2$ at 295–365 °C.

Experimental

Synthesis of the Ligands

3,3′,5,5′-tetramethyl-4,4′-bi-1H-pyrazole (tmbpz) was prepared as described by Mosby [21]. In a first step 3,4-diacetylhexane-2,5-dione was obtained by reaction of acetylacetone with sodium hydride and iodine in diethylether in a N_2 atmosphere. In a second step the diketone was reacted with hydrazine hydrate. The spectral data (i.r. and ^1H NMR) of diketone and ligand have been previously reported [5].

4,4′-methylene-bis-4,4′-bis-1H-pyrazole (mbpz) was synthesized as reported by Trofimenko [22] by reaction of pyrazole with CH_2Br_2 at 200 °C.

3,3′,5,5′-tetramethyl-4,4′-methylene-bis-1H-pyrazole (tmmbpz) was prepared by a two-step synthesis. In a first step 3,5-diacetyl-heptane-2,6-dione was prepared by the method described by Knövenagel [23], but modified as follows:

To a solution of acetylacetone (0.2 mol) and formaldehyde (0.24 mol) four drops of diethylamine were added under vigorous stirring in an ice bath. The reaction mixture was stirred for 24 hr at room temperature and during the following five days four drops of diethyl amine were added daily. After reaction the aqueous layer was separated and the organic one was diluted with diethyl-ether and dried with $MgSO_4$. When this solution was cooled in a dry ice–acetone bath a solid precipitated, which was filtered off at low temperature. The substance isolated melts at room-temperature to give a yellow oil, which is chromatographically pure (yield 94%).

In a second step a solution of 3,5-diacetyl-heptane-2,6-dione (38 mmol) in ethanol (10 ml) was added gradually to 11.3 ml of hydrazine hydrate (98%) at room temperature with stirring. The reaction mixture was refluxed for 45 min and stirred at room temperature for 18 hr. The solid formed was filtered off, washed with water and dried *in vacuo* (yield 67%, m.p. 276–278 °C). The spectral data (i.r. and ^1H NMR) of ligand and diketone have been previously reported [5].

Preparation of Complexes

Complexes of tmbpz

To a solution of tmbpz (2.6 mmol) in absolute ethanol (5 ml) at room-temperature was added a solution of the metal salt ($MCl_2 \cdot 6H_2O$ or $M(NO_3)_2 \cdot 6H_2O$, M = Co, Ni) (2.6 mmol), together with triethyl orthoformate (1.5 ml) as dehydration agent [24]. A coloured precipitate appeared when approximately half of the metal salt solution was added. After 18 hr stirring the precipitate was filtered off and recrystallized from absolute ethanol. Complexes of composition $CoCl_2(tmbpz)\cdot\frac{1}{2}H_2O$, $NiCl_2(tmbpz)_2 \cdot H_2O$, $Co(NO_3)_2(tmbpz)_2 \cdot H_2O$ and $Ni(NO_3)_2 \cdot H_2O$ were formed (yield 83–97% with respect to ligand). The reactions in molar ratio 1:2 (M:ligand) gave the same products with higher yields.

Complexes of tmmbpz

$MX_2(tmmbpz)_2 \cdot xH_2O$ complexes. To a solution of tmmbpz (2 mmol) in absolute ethanol (15 ml) was added a solution of the metal salt (chloride or nitrate) (1 mmol) in absolute ethanol (15 ml), together with triethyl orthoformate (0.6 ml) as dehydration agent and the reaction mixture was refluxed for ½ hr. A coloured precipitate was formed during reflux. After cooling at room temperature, the precipitate was filtered off and washed with dry diethyl-ether. $Co(NO_3)_2(tmmbpz)_2$, $NiCl_2(tmmbpz)_2$ and $Ni(NO_3)_2(tmmbpz)_2 \cdot H_2O$ were isolated in *ca.* quantitative yields.

$MCl_2(tmmbpz) \cdot xH_2O$. Complexes of composition $CoCl_2(tmmbpz)\cdot\frac{1}{2}H_2O$ and $NiCl_2(tmmbpz)$ were prepared as described for $CoCl_2(tmbpz)\cdot\frac{1}{2}H_2O$. The recrystallization from nitromethane/abs. ethanol yields deep blue crystals of composition $CoCl_2(tmmbpz)$ suitable for structure determination.

$Co(NO_3)_2(tmmbpz) \cdot H_2O$

To a solution of $Co(NO_3)_2 \cdot 6H_2O$ (1 mmol) in absolute ethanol (10 ml), cooled in an ice bath, 0.6 ml of ethyl orthoformate and the ligand (1 mmol) were added. A purple solution was formed. After 5 min stirring the solvent was eliminated *in vacuo*, petroleum ether was added to break the purple oil formed and the mixture was stirred for 24 hr. The resulting solid was filtered off and washed several times with petroleum ether (yield 98%).

Complexes of mbpz

Complexes of composition $MCl_2(mbpz)_2$ (M = Co, Ni) were prepared in *ca.* quantitative yields from 0.5 mmol of ligand by the method described above for the $MX_2(tmmbpz)_2$ complexes.

Physical Measurements

Conductivities were measured using a Philips PW 9506 digital conductivity meter. Infrared spectra were recorded as KBr disks or Nujol mulls in the 4000–500 cm^{-1} region and as Nujol mulls or polyethylene pressed disks in the 500–200 cm^{-1} region on a Perkin-Elmer 325 spectrophotometer. Ligand field spectra were obtained using a Kontron Uvikon 820 spectrophotometer fitted with a reflectance attachment (195–900 nm) and $BaSO_4$ as reference. Magnetic susceptibilities were measured on a standard Gouy or Faraday balance. The corrections for diamagnetism given by Selwood [25] were used. Carbon, hydrogen, nitrogen and chloro analyses were carried out by the Microanalysis Department of the Centro Nacional de Química Orgánica del CSIC (Madrid). The TG curves were recorded on a Dupont 900 thermobalance at a heating rate of 10 °C/min.

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References

1 S. Trofimenko, *Chem. Rev., 72,* 497 (1972).
2 F. Bonati, *Chim. Ind. (Milan), 62,* 324 (1980).
3 J. Reedijk and J. Verbiest, *Trans. Met. Chem., 4,* 239 (1979).
4 J. C. Jansen, H. van Koningsveld, J. A. C. van Ooycn and J. Reedijk, *Inorg. Chem., 19,* 170 (1980).
5 R. Uson, L. A. Oro, M. Esteban, A. M. Cuadro, P. Navarro and J. Elguero, *Trans. Met. Chem., 7,* 234 (1982).
6 J. G. Haasnot and W. L. Groeneveld, *Z. Naturforsch., 34b,* 1500 (1979).
7 N. A. Daugherty and J. W. Swisher, *Inorg. Chem., 7,* 1657 (1968).
8 C. W. Reimann, A. D. Mighell and F. A. Maurer, *Acta Cryst., 23,* 135 (1967).
9 J. Reedijk, *Recl. Trav. Chim. Pays-Bas, 89,* 605 (1970). *Ibid., 89,* 993 (1970).
10 M. J. Bagley, D. Nicholls and B. A. Warburton, *J. Chem. Soc. A,* 2694 (1970).
11 W. J. Geary, *Coord. Chem. Rev., 7,* 81 (1971).
12 B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.,* 338 (1959).
13 C. Foces-Foces, F. H. Cano and S. García-Blanco, *Acta Cryst.* (in press).
14 B. N. Figgis, M. Gerloch, J. Lewis, F. E. Mabbs and G. A. Webb, *J. Chem. Soc. A,* 2086 (1968).
15 A. B. P. Lever, E. Mantovani and B. S. Ramaswamy, *Can. J. Chem., 49,* 1957 (1971).
16 B. N. Figgis, *Trans. Faraday Soc., 56,* 1553 (1960).
17 C. W. Reimann, *J. Phys. Chem., 74,* 561 (1970).
18 P. J. McCarthy and J. Reedijk, *Inorg. Chim. Acta, 40,* 239 (1980).
19 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds', Wiley, New York, 1978.
20 J. Reedijk, *Recl. Trav. Chim. Pays-Bas, 90,* 117 (1971).
21 W. L. Mosby, *J. Chem. Soc.,* 3997 (1957).
22 S. Trofimenko, *J. Am. Chem. Soc., 92,* 5118 (1970).
23 E. Knövenagel, *Chem. Ber., 36,* 2136 (1903).
24 P. W. N. M. van Leeuwen and W. L. Groeneveld, *Inorg. Nucl. Chem. Lett., 3,* 145 (1967).
25 P. W. Selwood, 'Magnetochemistry', Interscience, New York, (1956).