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Transition-metal Compounds of Two Tetradentate Pyrazole Derivatives of Piperazine

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Abstract

The synthesis and characterization of transition-metal coordination compounds containing the newly synthesized ligands *N,N'*-bis(3,5-dimethylpyrazol-1-ylmethyl)piperazine (abbreviated chbd) and *N,N'*-bis(pyrazol-1-ylmethyl)piperazine (abbreviated chbp) are described. Most chbd compounds have the general formula $M_2(chbd)X_4$ (M = Cu, Zn, Mn, Cd with X = Cl; M = Cu, Zn with X = Br; and M = Cu with X = NO_3, SCN). The mixed-ligand compound Cd(chmd)(dmpz)$(NO_3)_2$, in which chmd stands for *N*-(3,5-dimethylpyrazol-1-ylmethyl)piperazine and dmpz stands for 3,5-dimethylpyrazole, is formed from the partially hydrolyzed ligand chbd. Complexes with chbp have the formulas M(chbp)X (M = Cu; X = Cl), $M(chbp)X_2$ (M = Zn; X = Cl, Br) and $M_2(chbp)X_3$ (M = Cu, Zn; X = Cl, Br). All compounds have been characterized by a combination of several spectroscopic methods. In all compounds chbd and chbp act as tetradentate ligands. In all cases the anions are coordinated to the metal ions. With chbd only dinuclear compounds are formed. With chbp both mononuclear and dinuclear compounds are formed.

Introduction

To obtain insight into the correlation between structure and nature of metalloenzymes, low-molecular weight coordination compounds may be used to model [1, 2] and, eventually, to mimic these metalloproteins. Recently, a new method for the synthesis of a large variety of *N*-substituted pyrazole derivatives was described [3], which provides routes to a variety of examples of interesting model systems. The pyrazole derivatives of simple amines, for example ammonia [4], aminoethane [5], and aniline [6], have already been the subject of research. The insight gained into the function and properties of the compounds may be a good base for studies of more complex chelating systems.

To study the effect of steric factors in such chelating ligands two ligands have been selected, which were expected to coordinate with four nitrogen donor atoms to one metal ion (mononucleating tetradentate chelating ligands). In this paper the coordination behaviour of the ligands, *N,N'*-bis(3,5-dimethylpyrazol-1-ylmethyl)piperazine, abbreviated chbd, and *N,N'*-bis(pyrazol-1-ylmethyl)piperazine, abbreviated chbp, towards divalent transition metals is described (see Fig. 1). These ligands contain four nitrogen donor atoms, *i.e.* two amine nitrogens and two pyrazole nitrogens, in an orientation, which could allow chelation to one metal ion. According to molecular models this orientation could be hampered for the ligand chbd by substantial sterical hindrance of the two methyl groups on each pyrazole. For the ligand chbp sterical hindrance will not take place because of the absence of substituents on the pyrazole rings. Compounds of divalent transition metals with the dimethylpyrazole derivative of *N,N'*-dimethylethylenediamine (debd) as ligand have an octahedral coordination geometry [7], with two *cis*-oriented anions. The constraint in the ligands chbd and chbp is expected to be larger than the constraint in debd. It was therefore hardly predictable whether chbd and chbp would act as mononucleating tetradentate chelating ligands, or whether other coordination geometries would be observed.

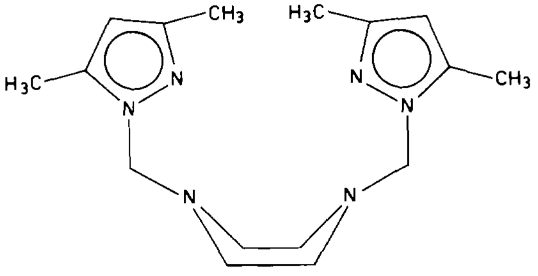

Fig. 1. One of the possible conformations of the ligand *N,N'*-bis(3,5-dimethylpyrazol-1-ylmethyl)piperazine (chbd).

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Experimental

Ligand Syntheses

The ligand *N,N'*-bis(3,5-dimethylpyrazol-1-ylmethyl)piperazine was synthesized following the procedure described earlier [3]: 24.20 g (0.19 mol) *N*-hydroxymethyl-3,5-dimethylpyrazole (nhdp) was added to a suspension of 8.26 g (0.096 mol) piperazine in 200 ml acetonitrile. This solution was stirred for three days in an open vessel at room temperature. The ligand started crystallizing after five minutes from the addition of the *N*-hydroxymethyl-3,5-dimethylpyrazole. The product was collected by filtration and washed with acetonitrile and diethylether. The compound obtained was characterized by infrared and proton NMR. The ^{1}H NMR spectrum (solvent $CDCl_3$, reference $SiMe_4$) showed the following signals: singlets at 2.19 ppm (6H) and at 2.24 ppm (6H), representing the pyrazole methyl groups, a singlet at 4.61 ppm (4H), and at 5.74 ppm (2H), representing respectively the methylene bridges and the pyrazole hydrogens, and a triplet centered at 2.57 ppm (8H), representing the piperazine hydrogens.

The ligand *N,N'*-bis(pyrazol-1-ylmethyl)piperazine was synthesized following the same procedure as used for the synthesis of the ligand *N,N'*-bis(3,5-dimethylpyrazol-1-ylmethyl)piperazine [3]: 13.5 g (0.14 mol) *N*-hydroxymethylpyrazole (abbreviated nhpz) was added to a suspension of 5.93 g (0.068 mol) piperazine in 150 ml acetonitrile. This solution was stirred for 24 h in an open vessel at room temperature. An intermediate product started crystallizing after five minutes from the addition of the *N*-hydroxymethylpyrazole. This precipitate dissolved overnight during stirring. After removing part of the solvent *in vacuo* on a rotatory evaporator the solution was stored at –20 °C to crystallize. The product was collected by filtration and washed with cold acetonitrile. The compound obtained was characterized by infrared and proton NMR. The ^{1}H NMR spectrum (solvent DMSO, reference $SiMe_4$) showed the following signals: a singlet at 4.85 ppm (4H), representing the methylene bridges; doublets at 7.42 ppm (2H) and at 7.67 ppm (2H), representing the outer pyrazole hydrogens; and triplets centered at 2.45 ppm (8H) and at 6.23 ppm (2H), representing respectively the piperazine hydrogens and the central pyrazole hydrogens.

Syntheses of Coordination Compounds

Except for copper thiocyanate, all other inorganic chemicals were commercially available, of sufficient purity, and used without further treatment. The coordination compounds with chbd were prepared by dissolving the hydrated metal salt (5 mmol) in 25 ml methanol and adding this solution to a solution of the ligand chbd (2.5 mmol) in 25 ml methanol. Occasionally triethylorthoformate was added for dehydration to both solutions before combining them. The $Cu(SCN)_2$ compound was prepared through a different procedure: $Cu(SCN)_2$ was synthesized from 5 mmol $Cu(NO_3)_2$ and 10 mmol NH_4SCN as published [8]. The resulting black powder was immediately added to a solution of 2.5 mmol of the ligand in 50 ml methanol. In the case of the cobalt and nickel salts, and of zinc nitrate, no well-defined products could be isolated. In some cases ligand decomposition took place, in other cases no solid crystalline products could be isolated at all. With cadmium nitrate the ligand loses one dimethylpyrazole group as shown by ^{1}H NMR. This dimethylpyrazole group is also present in the resulting complex. In spite of several attempts, no chbd complexes could be isolated containing the non-coordinating tetrafluoroborate anion.

The coordination compounds with chbp were prepared in various ways. The compounds, which contain two metal ions per molecule chbp (M = Cu, Zn; X = Cl, Br), were prepared by dissolving the ligand chbp (2.5 mmol) in 25 ml ethanol and adding this solution to a solution of the hydrated metal salt (5 mmol) in 25 ml ethanol. In the case of the zinc compounds tetrahydrofuran was used as solvent instead of ethanol. The compounds, which contain one divalent metal ion per molecule chbp (M = Zn; X = Cl, Br), were synthesized by dissolving the hydrated metal salt (2.5 mmol) in 25 ml ethanol and adding this to a solution of the ligand chbp (2.5 mmol) in 25 ml ethanol. In the case of zinc bromide tetrahydrofuran was used as solvent instead of ethanol. The copper(I) chloride compound was prepared by adding solid copper(I) chloride (2.5 mmol) to a solution of the ligand chbp (2.5 mmol) in 50 ml of a mixture (1:4) of acetonitrile and methanol. The suspension was stirred and warmed for one hour. The precipitated product was collected by filtration and washed with methanol. Occasionally triethylorthoformate was added for dehydration to the solutions. In the case of cobalt chloride, cobalt bromide and nickel chloride decomposition of the ligand took place and no pure products were isolated.

Characterization

Metal analyses were carried out complexometrically using EDTA as complexing agent [9]. Halogen analyses were carried out complexometrically using $AgNO_3$ as precipitating agent [10]. C, H and N analyses were performed at University College, Dublin, Ireland.

Infra-red spectra were recorded on a Perkin-Elmer 580 spectrophotometer as Nujol mulls between NaCl discs (4000–600 cm^{-1}) and polyethylene discs (600–180 cm^{-1}) and as KBr pellets (4000–200 cm^{-1}).

Solid-state electronic spectra (28 000–5 000 cm^{-1}) were recorded on a Perkin-Elmer 330 spectrophotometer fitted with a reflectance attachment.

TABLE I. Colours, Metal Analyses, Melting Points, Infrared and X-ray Types and Tentative Values of Infrared Metal–Halogen Stretching Vibrations of the Complexes with chbd and chbp. Calculated Values of Metal Analyses are in Parentheses.

Compound	Colour	Metal analysis (%)	Melting point[a]	IR-type[b]	X-ray type[c]	M–X band[d]
$Zn_2(chbd)Cl_4$	white	22.9(22.7)	208	A	I	310
$Zn_2(chbd)Br_4$	white	17.0(17.4)	215	A	I	260
$Cu_2(chbd)Cl_4$	green	22.2(22.3)	145	B	–	325
$Cu_2(chbd)Br_4$	brown	16.9(17.0)	153	B	II	–
$Cu_2(chbd)(NO_3)_4$	blue	19.6(18.8)	311	B	–	–
$Cu_2(chbd)(SCN)_4$	green	18.6(19.2)	154	C	III	–
$Mn_2(chbd)Cl_4$	pink	19.9(19.8)	267	C	IV	310
$Cd_2(chbd)Cl_4$	white	32.0(33.6)	284	C	V	–
$Cd(chmd)(dmpz)(NO_3)_2$	white	21.2(21.3)	190	D	VI	–
$Zn(chbp)Cl_2$	white	18.1(17.1)	182	E	VII	300
$Zn_2(chbp)Cl_4$	white	24.8(25.2)	210	F	VIII	320
$Zn(chbp)Br_2$	white	13.7(13.9)	178	E	IX	–
$Zn_2(chbp)Br_4$	white	18.0(18.8)	177	F	X	–
$Cu(chbp)Cl$	light green	19.5(18.4)	184	G	XI	–
$Cu_2(chbp)Cl_4$	green	24.2(24.7)	200	H	XII	330
$Cu_2(chbp)Br_4$	brown	17.6(18.3)	182	H	XIII	290

[a] All compounds show a small melting traject (less than 2 degrees). The highest values are given. [b] Same letter means similar infrared spectrum (position, relative intensity, shape). [c] Same Roman numeral means identical X-ray powder pattern. [d] Values in cm^{-1}. X = Cl, Br.

The conductivity of 10^{-3} mol dm^{-3} solutions of both zinc bromide chbp compounds in dimethylformamide, abbreviated dmf, ($K = 7.6 \times 10^{-7}$ ohm^{-1} cm^{-1}) was measured at 25 °C on a Philips PR 9500 conductometer.

ESR spectra were measured as powdered compounds with the use of a Varian V4500 Q-band spectrophotometer at 77 K (liquid nitrogen) and a Varian E3 X-band spectrophotometer at room temperature and at 77 K (liquid nitrogen).

Proton nuclear magnetic resonance spectra were recorded on a JEOL PS-100 instrument employing a frequency of 99.5 MHz, using $SiMe_4$ as internal standard.

X-ray powder diagrams of the compounds were obtained with a Guinier-type camera using Cu $K\alpha$ radiation. The samples were protected from atmospheric vapur by adhesive tape.

Results and Discussion

General

Colours, metal analyses, melting points, infrared and X-ray types, and tentative values of infrared metal–halogen stretching vibrations of the compounds with chbd and chbp are given in Table I. In Tables II and III ligand-field absorption bands and X-band EPR data are listed. For halogen analyses, full elemental analyses of some representative compounds, and NMR chemical shift values see 'Supplementary Material'. The analytical data are in agreement with the calculated values. The NMR chemical shift values are in agreement with those of the corresponding ligands. Many details in the infrared spectra of the complexes are characteristic for pyrazole derivatives [11, 12]. Strong infrared similarities are observed for several compounds (see Table I). X-ray powder isomorphism is found only for the zinc chloride and bromide chbd compounds. All other complexes have mutually different X-ray powder diffraction patterns (see Table I). This means, that despite the IR similarities, which indicate a very similar conformation of the ligand, the packing in the complexes can be quite different from one another. Unfortunately, several attempts to grow single crys-

TABLE II. Ligand-field Absorption Bands (cm^{-1})

Compound	Band values
$Cu_2(chbd)Cl_4$	13600; 24800
$Cu_2(chbd)Br_4$	14100; 21400
$Cu_2(chbd)(NO_3)_2$	14500
$Cu_2(chbd)(SCN)_4$	15200; 23100
Cu-dope in $Zn_2(chbd)Br_4$	14900; 17300
Cu-dope in $Cd_2(chbd)Cl_4$	12500; 26600
Cu-dope in $Cd(chmd)(dmpz)(NO_3)_2$	14600
$Cu_2(chbp)Cl_4$	12600
$Cu_2(chbp)Br_4$	12800
Cu-dope in $Zn(chbp)Br_2$	11300
Cu-dope in $Zn_2(chbp)Br_4$	14300

TABLE III. ESR Parameters of the Copper Compounds and of Copper Dopes in Zinc and Cadmium Compounds

Compound	Temperature	$g_\perp$	$g_\parallel$	$A_\parallel$[a]
$Cu_2(chbd)Cl_4$	room	2.09	2.16	78
$Cu_2(chbd)Br_4$	liquid N_2	2.07	2.30	75
$Cu_2(chbd)(NO_3)_4$	liquid N_2	2.07	2.35	136
$Cu_2(chbd)(SCN)_4$	room	2.09	2.21	
$Zn_2(chbd)Br_4$	room	2.07	2.22	175
$Cd_2(chbd)Cl_4$	room	2.07	2.29	115
$Cd(chmd)(dmpz)(NO_3)_2$	room	2.07	2.30	143
$Cu_2(chbp)Cl_4$	room	2.07	2.24	
$Cu_2(chbp)Br_4$	room	2.07		
$Zn(chbp)Cl_2$	room	2.08	2.24	169
$Zn(chbp)Br_2$	liquid N_2	2.07	2.28	140
$Zn_2(chbp)Br_4$	room	2.04	2.22	175

[a] Values in Gauss.

tals of one of these compounds have remained unsuccessful.

With the cobalt, nickel and iron chlorides, the cobalt and nickel nitrates, the cobalt bromide, the copper azide and the zinc tetrafluoroborate no compound with chbd could be isolated. In these cases decomposition of the ligand into nhdp and dmpz occurred. For the same reason dopes of copper in the zinc chloride chbd compound and of cobalt in the zinc bromide chbd compound could not be obtained pure. The instability of the ligand in the presence of Lewis acids is also reflected in the composition of the cadmium nitrate compound, where part of the ligand decomposed to dmpz.

With the pyrazole derivative of piperazine, chbp, no compounds with cobalt and nickel chloride and cobalt bromide could be isolated. Just as in the case of chbd decomposition of the ligand occurred. For the same reason a dope of copper in the zinc chloride compound, which contains two metal ions per molecule chbp, could not be synthesized.

In all isolated chbd complexes the metal to ligand ratio is two to one. When chbd would have acted as a mononucleating tetradentate ligand the metal to ligand ratio would have been one to one. Evidently, chbd cannot act as a mononucleating tetradentate ligand. The constraint in the ligand and the sterical hindrance, caused by the methyl pyrazole groups, are apparently too large to permit such a behaviour of the ligand chbd.

With chbp both the ratios two to one and one to one occur. In the compounds with a one to one ratio (M = Zn, Cu with X = Cl; M = Zn with X = Br) chbp can act as a mononucleating tetradentate ligand. Such a conformation of chbp will not be obstructed by sterical hindrance, since the methyl pyrazole groups are absent.

In all chbd and chbp complexes with a metal to ligand ratio of two to one, only two nitrogen atoms are available for each metal ion. In these cases, chbd and chbp will act as dinucleating tetradentate ligands. This gives rise to four-coordination, when the anions also take part in the coordination. The metal ions, with which $M_2(chbd)(anion)_4$ (M = Cu, Zn, Mn, Cd) and $M_2(chbp)(anion)_4$ (M = Cu, Zn) compounds are isolated, are just those metal ions, which have some preference for a four-coordination, either with a tetrahedral or with a square planar geometry. Metal ions like nickel and cobalt show a stronger preference for octahedral or five-coordination, which in this case can only be reached when solvent molecules also participate in the coordination or when halide anions bridge between metal ions. This can be assumed to be energetically unfavourable, since complexes of nickel and cobalt with both ligands could not be isolated.

Spectroscopic Results

The infrared spectra of all compounds agree with the infrared spectra of the corresponding ligands. For the chbd and the chbp compounds pyrazole ring vibrations are found at 1550 and 1520 cm^{-1}, respectively. The values of the metal–halogen stretching vibrations of the zinc chloride and bromide chbd compounds and both zinc chloride chbp compounds are in agreement with those in tetrahedral four-coordinated zinc(II) halide compounds (see Table I) [13, 14]. In the infrared spectrum of the copper nitrate chbd compound weak absorption bands at 1725 and 1755 cm^{-1}, and strong adsorption bands at 1295 and 1460 cm^{-1} are observed. These values suggest a bidentate nitrate coordination towards the copper ion [15]. Likewise, weak vibrations at 1730 and 1770 cm^{-1}, and strong vibrations at 1285 and 1460 cm^{-1} in the spectrum of the cadmium nitrate chmd compound indicate that the nitrate groups are coordinated bidentately towards the cadmium ion [15]. CN stretching absorptions at 2070 and 2120 cm^{-1} in the infrared spectrum of the copper thiocyanate chbd compound are consistent with the presence of two coordinated thiocyanates per metal ion [16, 17]. Because of the occurrence of ligand bands in the same regions of the infrared spectrum, assignments of absorptions to other thiocyanato vibrations (bendings) cannot be made.

NMR chemical shift values of the zinc chloride, zinc bromide, and cadmium chloride chbd compounds agree with the spectral data of free chbd. NMR chemical shift values of all zinc chloride and zinc bromide chbp compounds agree with the spectral data of free chbp (See 'Supplementary Material'.) The NMR spectrum of the cadmium nitrate chbd compound demonstrates that in this compound part of the ligand decomposed by splitting off 3,5-dimethylpyrazole. Pyrazole hydrogen signals at 5.75 and 5.80 ppm are due respectively to dimethylpyrazole bound to piperazine, and to 'free' dimethylpyrazole. The methylene bridge hydrogen signal at 4.60 ppm corresponds with two instead of four hydrogens. The methyl pyrazole signals at 2.08 and 2.21 ppm point to the presence of six instead of twelve methyl pyrazole hydrogens. Finally, there is an extra signal at 2.16 ppm, corresponding with six methyl hydrogens of dimethylpyrazole. So the dimethylpyrazole to chmd ratio is one to one. An NMR spectrum of the copper(I) chloride chbp compound could not be obtained, since the complex did not dissolve sufficiently in one of the available solvents.

The position of the bands in the Vis–NIR spectrum of the copper dope in the zinc bromide chbd compound (see Table II) may also be indicative for a four-coordinated zinc(II) geometry. Coordination geometries of other compounds cannot be determined from the Vis–NIR spectra of these compounds.

EPR parameters of the copper compounds are listed in Table III. The spectrum of the copper bromide chbp compound shows an isotropic signal. Spectra of all other compounds are axial. $A_{\parallel}$-values of the copper halide chbd compounds are quite small, suggesting a near tetrahedral geometry [18, 19].

Electral conductance data of $Zn(chbp)Br_2$ and $Zn_2(chbp)Br_4$ are 8.7 and 14.9 $ohm^{-1}\ cm^2\ mol^{-1}$, respectively. These values indicate, that in both compounds the anions are coordinated to the metal ion [20].

Conclusion

In all cases the ligand chbd binds to two metal ions. Apparently the formation of mononuclear compounds, in which the ligand chbd acts as a mononucleating tetradentate ligand, is not favourable, probably due to the sterical hindrance caused by the pyrazole methyl groups. The ligand chbp binds in most cases to two metal ions, but also in some cases to only one metal ion. This means that, in contrast with the ligand chbd, mononuclear compounds occur with the ligand chbp, thereby acting as a mononucleating tetradentate ligand.

In most chbd compounds and in the chpb compounds with a metal to ligand ratio of two to one, the metal ions are coordinated by two ligand-nitrogens and two anions, resulting in a four-coordination. The metal ions in the copper and cadmium nitrate chbd compounds appear to be six-coordinated, as bidentate coordinating nitrate is present. In the zinc halide chbp 1:1 compounds the metal ions are probably coordinated by four ligand-nitrogens and two anions, resulting in a six-coordination. Due to metal-induced ligand-decomposition reactions, no pure Co(II) and Ni(II) compounds could be isolated with the present ligands.

Supplementary Material

Analytical and NMR data are available from the authors on request.

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References

1 S. Trofimenko, *Chem. Rev., 72,* 497 (1972).
2 J. Reedijk and J. Verbiest, *Transition Met. Chem., 4,* 239 (1979).
3 W. L. Driessen, *Recl. Trav. Chim. Pays-Bas, 101,* 441 (1982).
4 G. J. van Driel, W. L. Driessen and J. Reedijk, *Inorg. Chem., 24,* 2919 (1985).
5 J. W. F. M. Schoonhoven, W. L. Driessen, J. Reedijk and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.,* 1053 (1984).
6 H. L. Blonk, W. L. Driessen and J. Reedijk, *J. Chem. Soc., Dalton Trans.,* 1699 (1985).
7 F. Paap, W. L. Driessen, B. Kojic-Prodic, J. Reedijk and A. L. Spek, *Inorg. Chim. Acta, 104,* 55 (1985).
8 C. Claus, *Bl. Acad. Petersb., 4,* 195 (1838).
9 A. I. Vogel, 'Quantitative Inorganic Analyses', Longman, London, 1961.
10 W. Schoeniger, *Mikrochim. Acta,* 869 (1956).
11 W. L. Driessen and P. L. A. Everstijn, *Recl. Trav. Chim. Pays-Bas, 41,* 179 (1980).
12 J. Reedijk, *Recl. Trav. Chim. Pays-Bas, 90,* 117 (1971).
13 R. J. H. Clark, *Spectrochim. Acta, 21,* 955 (1965).
14 C. Postmus, J. R. Ferraro and W. Wozniak, *Inorg. Chem., 6,* 2030 (1967).
15 G. J. Kleywegt, W. G. R. Wiesmeijer, G. J. van Driel, W. L. Driessen and J. Reedijk, *J. Chem. Soc., Dalton Trans.,* 2177 (1985).
16 R. A. Bailey, S. L. Kozak, T. W. Michielsen and W. N. Mills, *Coord. Chem. Rev., 6,* 471 (1971).
17 M. Kabesova and J. Gazo, *Chem. Zvesti, 34,* 800 (1980).
18 D. C. Gould and A. Ehrenberg, *Eur. J. Biochem., 5,* 451 (1968).
19 U. Sakaguchi and A. W. Addison, *J. Am. Chem. Soc., 99,* 5189 (1977).
20 R. K. Boggess and D. A. Zatko, *J. Chem. Educ., 52,* 649 (1975).