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Transition metal complexes of two related pyrazole containing ligands: 3,6-dimethyl-1,8-(3,5-dimethyl-1-pyrazolyl)-3,6-diazaoctane (ddad) and 1,4-bis(2-ethyl-(3,5-dimethyl-1-pyrazolyl))-piperazine (bedp). Synthesis, spectroscopy and X-ray structures

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Abstract

Several coordination compounds with the ligand 3,6-dimethyl-1,8-(3,5-dimethyl-1-pyrazolyl)-3,6-diazaoctane (ddad) were obtained: (Cu, Ni)(ddad)$(BF_4)_2$, Co(ddad)$(H_2O)(BF_4)_2$, (Co, Ni, Cu, Zn)$_2$(ddad)Cl_4, Co_3(ddad)$_2(NCS)_6$ and Cu_2(ddad)$(NCS)_3$. Five X-ray structures were obtained, viz. of [Cu(ddad)]$(BF_4)_2$, [Ni(ddad)]$(BF_4)_2$, Ni(ddad)$(NCS)_2$, [Ni(bedp)]$(H_2O)(BF_4)_2$ and [Cu(bedp)]$(H_2O)(BF_4)_2$, but the data did not allow the calculation of very accurate bond lengths. However, the basic coordination geometries were obtained in all cases. The coordination by the ligands is square planar, while Ni(ddad)$(NCS)_2$ contains additional *trans* coordinating thiocyanate anions. The asymmetric unit of [Cu(ddad)]$(BF_4)_2$ contains two almost identical $[Cu(ddad)]^{2+}$ species. The coordination of the copper atoms in both molecules is intermediate between tetrahedral and square planar. One molecule $[Cu(ddad)]^{2+}$ is the (*R*, *R*) diastereoisomer of the ligand and the other is the (*S*, *S*) diastereoisomer. The chloride compounds are, except for Ni(II), all dinuclear with MN_2Cl_2 chromophores. The nickel(II) compound contains square planar $Ni(ddad)^{2+}$ cations and tetrahedral $NiCl_4{}^{2-}$ anions. The thiocyanate compound of Ni(II), which is isomorphous with the corresponding Zn(II) compound, has octahedral $MN_2N_2'N_2''$ chromophores. The cobalt compound crystallizes as $[Co(ddad)(NCS)]_2Co(NCS)_4$ with five coordinate cobalt in the cation. With copper thiocyanate ddad forms the mixed-valence compound Cu_2(ddad)$(NCS)_3$, with $[Cu(ddad)]^{2+}$ and $[Cu(NCS)_3]^{2-}$. With the ligand, 1,4-bis(2-ethyl-(3,5-dimethyl-1-pyrazolyl))-piperazine (bedp) the compounds [(Ni, Cu)(bedp)]$(H_2O)(BF_4)_2$, (Ni, Co)(bedp)$(NCS)_2$, Zn_2(bedp)$(NCS)_4$, (Ni, Co, Cu, Zn)$_2$(bedp)Cl_4 and Cu_2(bedp)$(NCS)_3$ were obtained. The chloride compounds form dinuclear compounds (similar to ddad) with MN_2Cl_2 chromophores. However, in addition to the green form of [Ni(bedp)][$NiCl_4$] a purple isomer Ni_2(bedp)Cl_4, with a tetrahedral NiN_2Cl_2 chromophore, was obtained. The ligand field spectra of Ni(bedp)$(NCS)_2$ and the isomorphous cobalt compound show typical octahedral chromophores. With copper thiocyanate a mixed-valence compound was formed, with a structure likely to be similar to the corresponding ddad compound, viz. [Cu(II)(bedp)][Cu(I)$(SCN)_3$].

Introduction

The use of low-molecular weight coordination compounds as models for the active site of metalloproteins has gained much attention in recent years. In our programme dealing with the type I copper site [1], a synthetic route towards ligands containing pyrazole groups in combination with thioether donor functions was developed [2]. Ligands containing aliphatic nitrogen donor atoms in combination with the pyrazole groups have also been developed [3] to model the active sites of metalloproteins, like carboxypeptidase and superoxide dismutase, and to obtain a better understanding of the coordination behaviour of this type of ligands.

Two such ligands, viz. *N*,*N*′-bis(3,5-dimethylpyrazolyl-1-ylmethyl)piperazine (chbd) and 1,6-bis(3,5-

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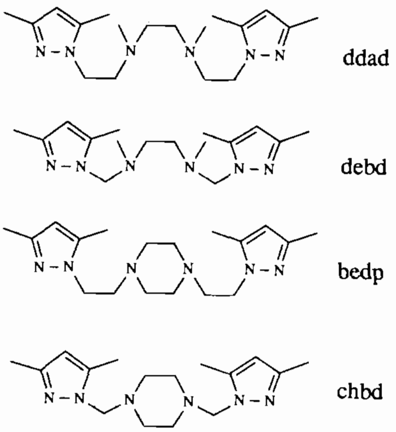

Fig. 1. Schematic drawing of the ligands ddad, debd, bedp and chbd.

dimethylpyrazol-1-yl)-2,5-dimethyl-2,5-diazahexane (debd), are depicted in Fig. 1. The steric constraints of the ligand debd greatly influence its coordination chemistry [4]. With the ligand chbd the pyrazole methyl groups and the short bridge between the two types of nitrogen donors apparently hamper the formation of mononuclear compounds [5].

Using the new synthetic route [2] it appeared possible to synthesize the ligands 3,6-dimethyl-1,8-(3,5-dimethyl-1-pyrazolyl)-3,6-diazaoctane (ddad) and 1,4-bis(2-ethyl-(3,5-dimethyl-1-pyrazolyl))-piperazine (bedp), also depicted in Fig. 1, which are similar to chbd and debd. The main difference between debd and chbd on the one hand and ddad and bedp on the other hand is the length of the bridge between the pyrazole group and the aliphatic nitrogen donor allowing six-membered and five-membered chelate rings, respectively. For ddad and bedp this bridge is one methylene group longer and, therefore, these ligands are more flexible. Because of the interesting results obtained [4, 5] with the ligands debd and chbd, and the introduction of more flexibility in the bridge segment, the coordination behaviour of the ligands ddad and bedp towards several transition metal salts was investigated. The results, including a few X-ray structures, are described below.

Experimental

Starting materials

All chemicals and solvents were commercially available and used without further purification. The preparation of *p*-tosyl-1-(2-hydroxyethyl)-3,5-dimethylpyrazole (ptos-N-hed) from commercially available starting materials has been described in detail elsewhere [2]. The ^{1}H NMR spectrum of ptos-N-hed shows the following signals: (solvent $CDCl_3$, internal standard TMS) 7.60 (d, 2H), 7.04 (d, 2H), 5.68 (s, 1H), 4.20 (m, 4H), 2.44 (s, 3H), 2.16 (d, 6H).

Synthesis of the ligands ddad and bedp

The synthesis of the ligands was undertaken by a variation of the method reported earlier [2].

3,6-Dimethyl-1,8-(3,5-dimethyl-1-pyrazolyl)-3,6-diazaoctane (ddad)

The tosylated 1-(2-hydroxyethyl)-3,5-dimethyl-pyrazole was added to a solution of NaOH and *sym*-dimethylethylenediamine in 100 ml of H_2O. The solution was refluxed for 5–6 h then allowed to cool slowly with stirring. An off-white material was obtained which was recrystallized from ethanol to produce a white solid. The ^{1}H NMR spectrum shows the following signals (solvent $CDCl_3$, internal standard TMS): 2.18 (d, 12H), 2.24 (s, 6H), 2.43 (s, 4H), 2.67 (t, 4H), 3.97 (t, 4H), 5.69 (s, 2H) ppm.

1,4-bis(2-ethyl-(3,5-dimethyl-1-pyrazolyl))-piperazine (bedp)

50 g (0.17 mol) ptos-N-hed was refluxed in 250 ml H_2O with 6.9 g (0.08 mol) piperazine and 7 g NaOH (0.175 mol), for about 4 h. After extraction of the reaction mixture with $CHCl_3$ and treatment with active charcoal the product was recrystallized from diethyl ether. Yield 13 g (49%). The ^{1}H NMR spectrum of the ligand bedp shows the following signals (solvent $CDCl_3$, internal standard TMS): 5.78 (s, 1H), 4.07 (t, 2H), 2.73 (t, 2H), 2.50 (s, 4H), 2.22 (s, 3H), 2.20 (s, 3H) ppm.

Synthesis of the coordination compounds

The compounds with the M(II) salts (Ni, Co, Cu, Zn)(Cl, NCS, BF_4)$_2$ were prepared by adding a hot solution of 2 mmol of the appropriate metal salt in 10 ml of absolute ethanol to a stirred hot solution of 2 mmol ligand in about 20 ml of absolute ethanol. About 2 ml of triethylorthoformate was then added for dehydration. To obtain the thiocyanates, the corresponding metal nitrate salt and an equivalent amount of NH_4NCS were solved in ethanol and then added to the ligand solution. Subsequent cooling to room temperature usually resulted in the crystallization of the coordination compounds in sufficient yields for analysis. When no solid compound could be isolated, acetonitrile or methanol were used as the solvent instead of ethanol. With the ligand bedp no solid coordination compound could be obtained with zinc and cobalt tetrafluoroborate, and with ddad no coordination compound with zinc thiocyanate could be obtained. Metal-doped complexes were prepared by starting from a mixture of the appropriate metal salts: 2–5% of the guest compound on molar scale, relative to the host compound.

Characterization procedures

IR spectra in the 4000–300 cm^{-1} range of the ligands ddad and bedp and of their coordination compounds pelleted in KBr were recorded on a Perkin-Elmer 580 spectrophotometer, equipped with a PE data station. Electronic spectra (270–2000 nm), using the diffuse reflectance method with MgO as reference, were obtained with a PE 330 spectrophotometer, also equipped with a PE data station. X-ray powder diagrams of the compounds were obtained with a Guinier type camera using Cu Kα radiation. After destruction with nitric acid, metal analyses were carried out complexometrically with edta [6]. EPR spectra were measured as powdered compounds or as frozen solutions on a Varian E3 X-band spectrophotometer at 77 K (liquid nitrogen). NMR measurements on [Ni(bedp)](H$_2$O)(BF$_4$)$_2$, dissolved in CD$_3$CN, along a temperature traject were performed on a Bruker WM 300 instrument with CD$_3$CN as internal standard. Conductivity measurements on Cu$_2$(bedp)(NCS)$_3$ in acetonitrile (10^{-3} M solutions) were performed with a Philips PW 9526 conductivity meter equipped with a PW 9551/60 PT 100 electrode with automatic temperature correction. Magnetic measurements (77–300 K) on the powdered samples were performed by the Faraday method on a locally built set, based on a Mettler M21-balance and an Oxford Newport magnet type A. The proton nuclear magnetic resonance spectra were recorded on a Jeol PS-100 instrument employing a frequency of 99.5 MHz.

X-ray data collection and structure refinement

Suitable crystals were obtained of [Cu(ddad)](BF$_4$)$_2$, [Ni(ddad)](BF$_4$)$_2$, Ni(ddad)(NCS)$_2$, [Ni(bedp)](H$_2$O)(BF$_4$)$_2$ and [Cu(bedp)](H$_2$O)(BF$_4$)$_2$. The refinement did not yield satisfactory *R* values; however, the refined model is sufficiently accurate for the description of the metal-ion coordination. For details of the crystal data see 'Supplementary material'. The final *R* values of (R_w in parentheses) of the X-ray single crystal structure determination of [Cu(ddad)](BF$_4$)$_2$, [Ni(ddad)](BF$_4$)$_2$, Ni(ddad)(NCS)$_2$, [Ni(bedp)](H$_2$O)(BF$_4$)$_2$ and [Cu(bedp)](H$_2$O)(BF$_4$)$_2$ are 0.065 (0.070), 0.090 (0.116), 0.16 (0.17), 0.115 (0.176) and 0.106 (12.9) respectively. Tables of selected bond lengths and bond angles of the four X-ray structures as well as Figures are given in 'Results'.

Results

General

Colours, metal analyses, IR patterns and X-ray types, melting points and electronic absorption maxima of the coordination compounds obtained with ddad and bedp have been collected in Table 1. EPR data are summarized in Table 2. The analytical data are in agreement with the calculated values for the proposed structures of all compounds (see 'Supplementary material'). The IR spectra of all compounds clearly show the presence of the corresponding ligand. The results will be summarized according to the anion. The NMR results will be presented in a separate paragraph.

Single crystals of the compounds [Cu(ddad)](BF$_4$)$_2$, [Ni(ddad)](BF$_4$)$_2$, Ni(ddad)(NCS)$_2$, [Ni(bedp)](H$_2$O)(BF$_4$)$_2$ and [Cu(bedp)](H$_2$O)(BF$_4$)$_2$ were obtained, but their structure could not be solved in great detail. The results of the crystal structure determinations will therefore only be used to describe the metal-ion coordination.

X-ray structure of [Cu(ddad)](BF$_4$)$_2$

The asymmetric unit of the compound [Cu(ddad)](BF$_4$)$_2$ contains two structurally almost identical formula units (see Fig. 2). The coordination of the copper atoms in both molecules is intermediate between tetrahedral and square planar, as can be deduced from the angles summarized in Table 3, which are larger than 90° but smaller than 109°. The dihedral angle (40.5°) is however closer to 0° than to 90° (expected for tetrahedral geometry). The copper nitrogen bond lengths can be regarded as normal [8]. If N2 and N5 are taken to correspond to N50 and N20, respectively, then all copper nitrogen bond lengths and all angles around the copper atoms are equivalent within estimated standard deviations, with the exception of the N2–Cu–N22 angle of 97.1(6)°, which is slightly larger than the related N20–Cu–N32 angle of 94.9(5)°. On the other hand a significant difference is found in the conformation at the chiral nitrogen atoms, as expected from the chirality of the complex cation, one molecule [Cu(ddad)](BF$_4$)$_2$ is the (*R*,*R*) diastereoisomer and the other is the (*S*,*S*) diastereoisomer.

The tetrafluoroborate anions are considered as not coordinated, as the smallest Cu–F distance is 3.8 Å. Study of the packing revealed no other than normal van der Waals contacts between the cations and the anions.

The chlorides

Both ligands ddad and bedp form dinuclear coordination compounds M$_2$(L)Cl$_4$ with the metal chlorides, with almost identical spectroscopic properties.

TABLE 1. Colours, melting points, X-ray and IR isomorphism and electronic absorption maxima of the coordination compounds of bedp and ddad

Compound	X-ray/IR[a]	Colour	m.p.[b]	LF-maxima (10^3 cm^{-1})
$[Cu(bedp)](H_2O)(BF_4)_2$	I	purple	254d	28.1, 15.6
$[Ni(bedp)](H_2O)(BF_4)_2$	I	orange	235	21.3
$Ni_2(bedp)Cl_4$		green	205d	21.7, 15.2, 15.0, 14.2, 7.5[c]
$Ni_2(bedp)Cl_4$		purple	>260	19.2, 17.6, 10.0, 6.9
$Ni_2(bedp)Cl_4.xH_2O$		orange	70d	23.4, 20.2, 14.8, 13.6, 8.5
$Co_2(bedp)Cl_4$	IV	blue	>260	17.7, 15.1, 9.6, 7.7, 6.3
$Cu_2(bedp)Cl_4$		green	184	23.5, 15.8, 7.7(br)
$Zn_2(bedp)Cl_4$	IV	white	>260	
$Ni(bedp)(NCS)_2$	II	blue	240d	26.8, 16.7, 10.0
$Zn_2(bedp)(NCS)_4$		yellow	260d	
$Co(bedp)(NCS)_2$	II	purple	154	29.9, 20.5, 16.3
$Cu_2(bedp)(NCS)_3$		green	173	16.3, 14.3
$[Ni(ddad)](BF_4)_2$		orange	>240	20.9
$Co(ddad)(H_2O)(BF_4)_2$		purple	>240	20.0, 17.2, 12.0
$[Cu(ddad)](BF_4)_2$		green	230	25.0, 16.9, 12.3
$Zn(ddad)(BF_4)_2$		white	>240	
$Co_2(ddad)Cl_4$	III	blue	>240	18.0, 15.9, 10.2, 8.1, 6.4
$Ni_2(ddad)Cl_4$		green	140	21.3, 15.2, 14.1, 7.2[d]
$Cu_2(ddad)Cl_4$		green	152	24.4, 15.2, 7.7(br)
$Zn_2(ddad)Cl_4$	III	white	>240	
$Ni(ddad)(NCS)_2$		blue	>240	27.0, 16.9, 10.0(br)
$Co_3(ddad)_2(NCS)_6$		blue	105	21.1, 16.3, 11.9, 7.7(br)
$Cu_2(ddad)(NCS)_3$		green	110	15.6(br)

[a] IR and X-ray isomorphous compounds. [b] Melting point in °C, d for decomposition. [c] 21.7×10^3 cm^{-1} is due to the square planar $[Ni(bedp)]^{2+}$ cation. [d] 21.3×10^3 cm^{-1} is due to the square planar $[Ni(ddad)]^{+2}$ cation.

TABLE 2. EPR data of copper and copper-doped compounds of ddad and bedp

Compound	Temperature (K)	*g* values
$Cu(ddad)(BF_4)_2$	ambient	2.17, 2.09 (axial)
$Ni(ddad)(BF_4)_2$[a]	77	2.18, 2.03
$Cu_2(ddad)Cl_4$	77	2.30, 2.12, 2.06
$Cu_2(ddad)(NCS)_3$	ambient	2.10 (isotropic)
$Cu(bedp)(H_2O)(BF_4)_2$	77	2.20, 2.05
$Ni(bedp)(H_2O)(BF_4)_2$[b]	77	2.17, 2.05
$Cu_2(bedp)Cl_4$	77	2.23, 2.10
$Cu_2(bedp)(NCS)_3$	77	2.18, 2.05, 2.02

[a] Cu(II) doped, $A_\parallel = 197$ G and a superhyperfine of 15 G. [b] Cu(II) doped, $A_\parallel = 157$ G. No superhyperfine observed.

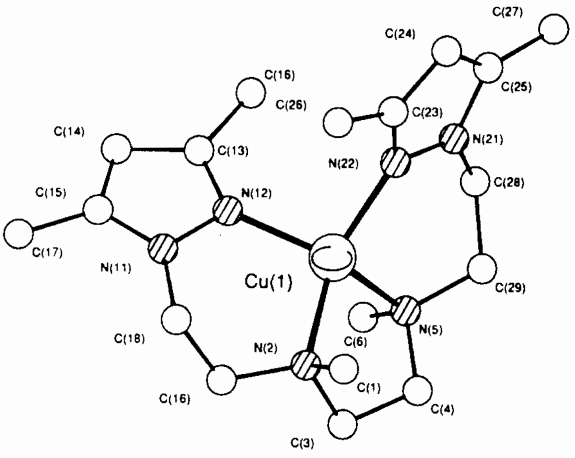

Fig. 2. Pluto drawing [7] of one of the $[Cu(ddad)]^{2+}$ cations of $[Cu(ddad)](BF_4)_2$. Hydrogen atoms are omitted for clarity.

The Co(II) and Zn(II) compounds are structurally isomorphous as deduced from the IR spectra and the X-ray powder patterns (see Table 1). The ligand field spectra of the compounds $Co_2(L)Cl_4$ clearly show a tetrahedrally coordinated CoN_2Cl_2 chromophore [9]. For the structurally isomorphous compounds $Zn_2(L)Cl_4$, the same chromophore can be assumed.

The ligand field spectra of the green Ni(II) compounds clearly show (Table 1) that two types of chromophores are present, a square planar (with LF-maximum at 21.7×10^3 cm^{-1} for bedp and 21.3×10^3 cm^{-1} for ddad) and a tetrahedral one.

TABLE 3. Selected bond lengths (Å) and bond angles (°) of [Cu(ddad)]$(BF_4)_2$ with standard deviations in parentheses

Cu(1)–N(2)	1.988(14)
Cu(1)–N(5)	1.996(14)
Cu(1)–N(12)	1.963(13)
Cu(1)–N(22)	1.951(13)
Cu(2)–N(20)	2.002(14)
Cu(2)–N(32)	1.965(13)
Cu(2)–N(42)	1.929(13)
Cu(2)–N(50)	2.003(13)
N(2)–Cu(1)–N(5)	87.2(6)
N(2)–Cu(1)–N(12)	98.3(5)
N(2)–Cu(1)–N(22)	145.3(6)
N(5)–Cu(1)–N(12)	143.2(5)
N(5)–Cu(1)–N(22)	97.1(6)
N(12)–Cu(1)–N(22)	98.5(5)
N(20)–Cu(2)–N(50)	86.9(6)
N(20)–Cu(2)–N(32)	94.9(5)
N(20)–Cu(2)–N(42)	143.6(6)
N(50)–Cu(2)–N(32)	145.2(6)
N(50)–Cu(2)–N(42)	98.4(6)
N(32)–Cu(2)–N(42)	100.3(5)

The electronic maxima of the tetrahedrally coordinated Ni(II) species are in good agreement with those reported for the species [9] $NiCl_4^{2-}$. The green colour of the compounds Ni_2(bedp)Cl_4 and Ni_2(ddad)Cl_4 apparently results from a combination of the square-planar NiN_4 chromophore (orange) and a tetrahedral $NiCl_4$ chromophore (blue). When the synthesis of Ni_2(bedp)Cl_4 is performed in an inert atmosphere and when freshly distilled acetonitrile is used, a purple coloured product, also analyzing as Ni_2(bedp)Cl_4, is obtained. The ligand field spectrum of this compound clearly shows the presence of only one Ni(II) species in a tetrahedral coordination geometry, and agrees with an NiN_2Cl_2 chromophore [9]. The IR spectrum and X-ray powder pattern of this purple coloured compound are, however, not identical to those of (Zn, Co)$_2$(bedp)Cl_4.

The green Ni_2(L)Cl_4 compounds are not stable in moist air. The compounds slowly turn orange and become slightly deliquescent. This behaviour appears to be reversible: when exposing the compounds to dry air or when storing them in *in vacuo* the green colour reappears. This cycle has been repeated several times. IR spectra [10] and metal analysis showed water to be absorbed during the colour change from green to orange. The ligand field spectrum of the orange product clearly shows the presence of two chromophores, a distinct square planar one, which must be due to the NiN_4 ligand^{2+} cation and an octahedral chromophore, presumably due to the $Ni(H_2O)_2Cl_4^{2-}$ anion [9].

The copper compounds of the two ligands ddad and bedp have very similar structures, according to their ligand field and EPR spectra, with, presumably, distorted tetrahedral CuN_2Cl_2 chromophores.

The thiocyanates

The coordination behaviour of the ligands ddad and bedp towards the thiocyanate containing metal salts, is different from the behaviour towards the metal chlorides. Only with bedp could a Zn(II) compound be obtained. The Ni(II) compounds of both ligands are structurally almost identical, showing the same formula Ni(L)$(NCS)_2$ and the same octahedral $NiN_4N'_2$ chromophore. This coordination geometry has been confirmed by the X-ray structure determination of Ni(ddad)$(NCS)_2$. The *R* values after the last refinement cycle of the crystal structure determination were 16 and 17%, due to twinning of the crystal. Although these *R* values are very high, the refined model is sufficiently accurate for a coordination chemistry description. Details of the X-ray structure determination can be found in 'supplementary material'. From the angles around the Ni(II) atom it is clear that the coordination deviates only slightly from ideal octahedral geometry (see Fig. 3 and Table 4). The thiocyanate anions are in a *trans* position and occupy the axial positions. The ligand coordinates through its four nitrogen donors to the nickel atom, which agrees with the position of the C–N vibration [10] in the IR spectrum. The bond lengths to the nickel atom can be regarded as normal [8] (see Table 4).

With Co(II) the ligands yield two different compounds. With ddad the compound Co_3(ddad)$_2$(NCS)$_6$ was obtained, and with bedp the compound Co(bedp)$(NCS)_2$ was isolated. In the latter compound, according to the ligand field spectrum, the Co(II) atom is octahedrally coordinated [9], most likely by four ligand nitrogen donors and by two thiocyanate nitrogen donors. The compound is structurally isomorphous with Ni(bedp)$(NCS)_2$, as de-

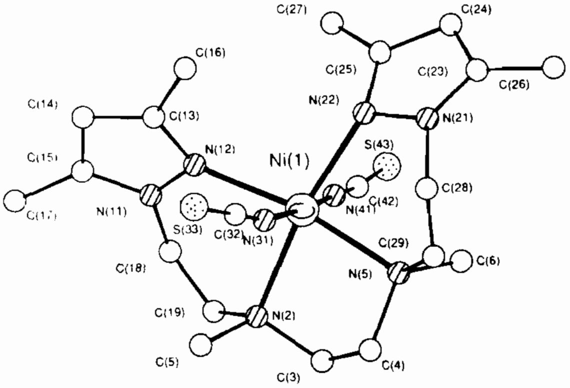

Fig. 3. Pluto drawing [7] of Ni(ddad)$(NCS)_2$. Hydrogen atoms are omitted for clarity.

TABLE 4. Selected bond lengths (Å) and bond angles (°) of Ni(ddad)$(NCS)_2$ with standard deviations in parentheses

Ni(1)–N2	2.16(2)
Ni(1)–N5	2.13(2)
Ni(1)–N12	2.17(2)
Ni(1)–N22	2.10(2)
Ni(1)–N31	2.06(2)
Ni(1)–N41	2.01(2)
N2–Ni(1)–N5	82.9(9)
N5–Ni(1)–N22	88.8(8)
N22–Ni(1)–N12	101.8(7)
N12–Ni(1)–N2	86.7(7)
N22–Ni(1)–N2	169.9(8)
N12–Ni(1)–N5	169.5(8)
N31–Ni(1)–N41	176.6(8)
Ni(1)–N31–C32	166(2)
Ni(1)–N41–C42	176(2)

duced from the X-ray powder photographs. The ligand field spectrum of the compound $Co_3(ddad)_2(NCS)_6$ shows the presence of two Co(II) species, one tetrahedral and one five coordinated [9]. The tetrahedral species is most likely the $[Co(NCS)_4]^{2-}$ complex anion [9, 11] and the other species thus $Co(ddad)(NCS)^+$, yielding the formula $[Co(ddad)(NCS)]_2Co(NCS)_4$.

The copper thiocyanate compounds of ddad and bedp are very similar; both are so-called mixed-valence compounds. This type of mixed-valence coordination compound of copper with thiocyanates with mostly polymeric-type structures has been reported before [12]. The EPR spectra of both compounds and a molar conductance of $Cu_2(bedp)(NCS)_3$ in CH_3CN of 138 S cm^2 mol^{-1}, corresponding to a 1:1 electrolyte, strongly suggest that these compounds are ionic, viz. consisting of a $Cu(L)^{2+}$ unit and a $[Cu(NCS)_3]^{2-}$ unit, although some NCS bridging in the solid state cannot be excluded.

With Zn(II) the only compound obtained is $Zn_2(bedp)(NCS)_4$; the structure could be dinuclear like the cobalt and nickel chloride compounds. The ligand field spectrum of the Co(II) doped compound (X-ray isomorphous to the undoped compound) clearly shows a tetrahedral Co(II) coordinated species, indicating that the compound $Zn_2(bedp)(NCS)_4$ is structurally very similar to the dinuclear (MN_2Cl_2) compounds.

The tetrafluoroborates

The metal(II) tetrafluoroborates of the ligands ddad and bedp also show very similar structures. The similarity in coordination behaviour is not quite reflected by the formulas of the compounds. The bedp compounds of copper and nickel tetrafluoroborate have an additional water molecule in the crystal lattice compared to the corresponding compounds of ddad which are anhydrous.

For the compounds $[Ni(ddad)](BF_4)_2$, $[Ni(bedp)](H_2O)(BF_4)_2$ and $[Cu(bedp)](H_2O)(BF_4)_2$ crystal structure determinations were undertaken. None of the three structure determinations resulted in satisfactory *R* values, however the coordination data are sufficiently accurate (see also 'Supplementary material').

In Ni(ddad)$(BF_4)_2$ the nickel atom is coordinated by two pyrazole nitrogens and two amine nitrogens in an almost regular square (see Fig. 4). The coordination angle spanned by the pyrazole-N-to-amine-N bite of the ligand is 90.1(2)° (see also Table 5). Restricted coordination angles of about 80° have so far always been encountered [3, 4] with pyrazole substituted amine ligands with only one methylene bridge between the pyrazole-N and the amine-N. The longer amine-to-pyrazole bridge in ddad apparently favors an ideal coordination angle of 90°. The slight distortion from a regular square must be due to the small bridge between both amine-nitrogens. The distances from the nickel ion to the pyrazole-N atom and to the amine-N atom are

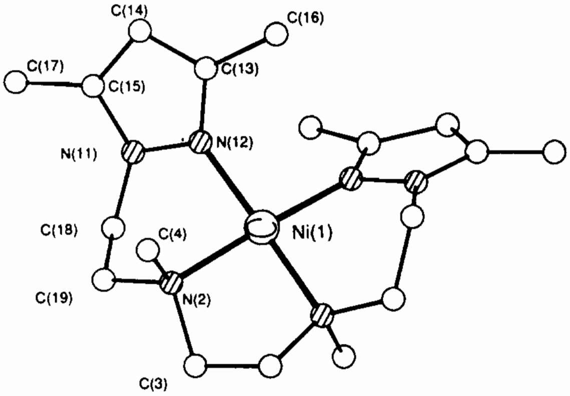

Fig. 4. Pluto drawing [7] of Ni(ddad)$(BF_4)_2$. Hydrogen atoms and anions are omitted for clarity.

TABLE 5. Selected bond lengths (Å) and bond angles (°) involving non-hydrogen atoms of $[Ni(ddad)](BF_4)_2$ with standard deviations in parentheses

Ni(1)–N(2)	1.949(6)
Ni(1)–N(12)	1.880(6)
N(2)–Ni(1)–N(12)	90.1(2)
N(2)–Ni(1)–N(2)*	87.9(4)
N(2)–Ni(1)–N(12)*	176.4(3)
N(12)–Ni(1)–N(12)*	92.0(3)
Ni(1)–N(2)–C(3)	107.8(4)
Ni(1)–N(2)–C(4)	106.3(5)
Ni(1)–N(2)–C(19)	116.4(5)
Ni(1)–N(12)–N(11)	119.8(4)
Ni(1)–N(12)–C(13)	133.8(5)

Asterisk (*) = ($\frac{1}{2}-x$, $\frac{1}{2}+y$, $+z$).

1.880(6) and 1.949(6) Å, respectively, which are comparable to metal to N distances in coordination compounds of related ligands [3, 4, 8]. There are no intramolecular distances shorter than the van der Waals distances; the crystal packing is, therefore, determined by normal van der Waals contacts.

As can be deduced from the X-ray powder photographs and the IR spectra (see Table 1), the two compounds $[Ni(bedp)](H_2O)(BF_4)_2$ and $[Cu(bedp)](H_2O)(BF_4)_2$ are structurally isomorphous. Because of the poor crystal quality of the Ni compound, the X-ray structure determination of a crystal of the copper compound was also undertaken. The crystals of the copper compound appeared to be of somewhat better quality ($R = 11$, $R_w = 13$) than those of the nickel compound ($R = 12$, $R_w = 18$).

The copper and nickel compounds are isomorphous, and the observed bond lengths and bond angles are summarized Table 6. Both compounds show very similar bond lengths and bond angles, and one drawing has been generated for both structures (see Fig. 5). The ligand bedp coordinates to the nickel and the copper atom in a square planar fashion (see Fig. 5). The coordination angles (see Table 6) show that the deviation from ideal square planar geometry is small. The distance between the oxygen of the water molecule and the nearest tetrafluoroborate anion is 2.97 Å, indicating that the water molecule is only weakly hydrogen bonded. The water molecule is separated by more then 5 Å from the metal ion, indicating that H_2O does not coordinate to the metal ion.

With the ligand ddad a compound with cobalt tetrafluoroborate was also obtained, viz. $Co(ddad)(H_2O)(BF_4)_2$. The ligand field spectrum agrees with five coordination of the cobalt(II) atom, indicating the chromophore [9] CoN_4O.

Magnetic properties and NMR spectroscopy of $[Ni(bedp)](H_2O)(BF_4)_2$

The ^1H NMR spectrum of a solution of the nickel compound in CD_3CN shows a number of very broad and shifted signals. Temperature variation experiments showed that this phenomenon is due to the presence of some paramagnetism. Addition of a small amount of H_2O to the sample results in a further broadening and an even larger shift of all signals. This leads to the conclusion that the paramagnetism is caused by a fast equilibrium on the NMR time-scale between the low-spin (diamagnetic) square-planar Ni(II)-N_4 and a high-spin (paramagnetic) five- or six-coordinated Ni(II)–$N_4(H_2O)_x$ species ($x = 1,2$). The magnetic moment of the solid-state nickel compound was therefore measured by the Faraday method. At room temperature this amounts to only 0.5 BM; temperature-independent paramagnetism is considered to be responsible for the very weak paramagnetism. The magnetic moment of the solution in acetonitrile was determined at room temperature with the Evans method [13]; a value of 2.14 BM was found. For a solid-state high-spin nickel compound with an octahedral coordination geometry a magnetic moment of 3.0–3.3 BM would be expected [14]. The magnetic properties are thus in agreement with the conclusion derived from the NMR measurements that in d^6-acetonitrile an equilibrium exists between the low-spin (diamagnetic) square-planar Ni(II)–N_4 and a high-spin (paramagnetic) five- or six-coordinated Ni(II)–$N_4(H_2O)_x$ species ($x = 1,2$).

The compound $Ni(ddad)(BF_4)_2$ shows a less broadened and hardly shifted NMR spectrum in CD_3CN; indeed this compound contains no crystal lattice water.

Discussion and concluding remarks

The results reported for the ligands ddad and bedp, described in this report, when compared to the ligands debd [4] and chbd [5] (see Fig. 1), show that there are striking differences in coordination behaviour. With the ligand debd, related to ddad, several X-ray structures are known, e.g. $Cd(debd)Cl_2$, $Ni(debd)(N_3)_2$ and $Cu(debd)(NCS)_2$. In these structures the coordinated anions are not placed in *trans*

TABLE 6. Bond lengths (Å) and bond angles (°) of the compounds $[Ni(bedp)](H_2O)(BF_4)_2$ and $[Cu(bedp)](H_2O)(BF_4)_2$ with e.s.d.s in parentheses

Bond length or angle	$[Ni(bedp)](H_2O)(BF_4)_2$	$[Cu(bedp)](H_2O)(BF_4)_2$
Ni(1)–N(04)	1.90(1)	2.064(16)
Ni(1)–N(12)	1.90(1)	1.974(14)
N(04)–Ni(1)–N(12)	93.8(5)	93.6(6)
N(04)–Ni(1)–N(04)*	78.3(7)	74.0(6)
N(04)–Ni(1)–N(12)*	167.2(5)	164.1(6)
N(12)–Ni(1)–N(12)*	95.6(8)	100.3(6)

Asterisk (*) = symmetry-related (twofold axis).

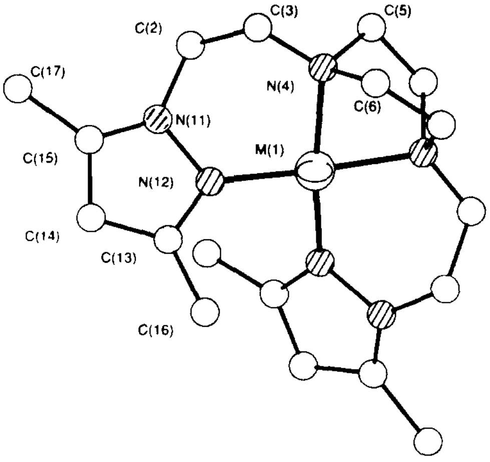

Fig. 5. Pluto drawing [7] of the $[M(bedp)]^{2+}$ cation with M is Cu or Ni. Hydrogen atoms are omitted for clarity.

positions but, in contrast to the structure of $Ni(ddad)(NCS)_2$, in *cis* positions. Thus the ligand debd coordinates not in the same square planar mode as ddad, which must be due to the greater flexibility of the pyrazole-to-nitrogen bridge segment.

For the ligand chbd no single crystal structures have been reported. The coordination compounds obtained with this ligand are all dinuclear compounds. No solid cobalt or nickel compounds could be isolated with chbd, nor any compounds with non-coordinating anions. The experiments undertaken to prepare nickel or cobalt compounds with chbd resulted in metal-induced ligand-decomposition [5]. In contrast bedp appeared to be more stable, and mononuclear compounds, compounds with the non-coordinating BF_4^- anion, and also compounds with cobalt and nickel were isolated. Most likely this difference is also related to the greater flexibility of bedp in comparison with chbd.

In the mononuclear compounds of ddad and bedp, except for $[Cu(ddad)](BF_4)_2$, the ligands act as tetradentate chelates, with a square-planar coordination mode. The coordination geometry of ddad in $[Cu(ddad)](BF_4)_2$ could not be determined exactly, but can best be described as distorted square planar. The difference in coordination between the ligands in the compounds $[Cu(ddad)](BF_4)_2$ and $[Cu(bedp)](H_2O)(BF_4)_2$ is interesting. The coordination in the first compound is clearly more distorted than in the second compound. This suggests that the piperazine ring of bedp forces the ligand in a square-planar coordination mode. The ligand ddad can therefore be regarded as less sterically constraint than the ligand bedp. Compared to $[Cu(ddad)](BF_4)_2$ the compound $[Cu(bedp)](H_2O)(BF_4)_2$ contains an additional crystal lattice water molecule, which is not coordinating to the copper atom. The structural difference between ddad and bedp, and thus a difference in crystal packing preferences, can be the origin for this variation.

Both ligands ddad and bedp form dinuclear compounds with metal ions and show thereby their capability of accepting, in principal, tetrahedral coordination geometries. This behaviour also demonstrates that both ligands are too sterically restricted to adapt a tetrahedral N_4 coordination mode on their own. The enlargement of the bridge pyrazole-N-to-amine-N segments in this type of ligand, on going from debd and chbd to bedp and ddad (see Fig. 1), apparently leads to ligand conformations which are able to adjust to octahedral or square-planar coordination geometries but not to a tetrahedral coordination geometry.

Supplementary material

A list of the analytical data and crystal structure determination data and tables of the fractional coordinates of $[Cu(ddad)](BF_4)_2$, $[Ni(ddad)](BF_4)_2$, $[Ni(ddad)(NCS)_2]$, $[Ni(bedp)](H_2O)(BF_4)_2$ and $[Cu(bedp)](H_2O)(BF_4)_2$ (in total 10 pages) are available from the authors on request.

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