Transition-metal Co-ordination Compounds of a Novel Aniline-based Pyrazole Derivative. *X*-Ray Crystal Structures of [*NN*-Bis(3,5-dimethylpyrazol-1-ylmethyl)aminobenzene]-dichlorocobalt(II) and -dibromocopper(II) †

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The synthesis and characterization of transition-metal co-ordination compounds containing the newly synthesized ligand *NN*-bis(3,5-dimethylpyrazol-1-ylmethyl)aminobenzene (bdmpab) are described. The compounds have the general formulae [M(bdmpab)X_2] (M = Co, Cu, or Zn; X = Cl or Br and M = Co; X = SCN or NO_3) and [Cu_2(bdmpab)$(SCN)_3$] and have been characterized by several spectroscopic methods and analytical techniques. In some compounds (*viz.* M = Co or Zn; X = Cl or Br and M = Co; X = SCN or NO_3) bdmpab acts as a bidentate ligand and in others (*viz.* M = Cu; X = Cl, Br, or SCN) as a tridentate ligand. In all compounds the anions are also bonded. Because of the flexible character of the ligand the preference of the transition-metal ions for specific co-ordination geometries is reflected in the resulting co-ordination compounds. To prove the chelating nature of the ligand, and in particular to find out whether or not the aniline nitrogen is co-ordinated, the crystal structures of two representative examples have been determined. [Co(bdmpab)Cl_2] crystallises in space group *Pbca*, with a = 8.713(2), b = 17.252(4), c = 27.626(7) Å, and Z = 8. Standard least-squares refinement gave R = 0.031 (R' = 0.028). The cobalt atom has a CoN_2Cl_2 chromophore in a distorted tetrahedral geometry. Co–N distances are 2.038(2) and 2.044(2) Å for the pyrazole nitrogens. The Co ··· N contact of 3.854(2) Å for the aniline nitrogen is considered as non-co-ordinating. Co–Cl distances are 2.2434(8) and 2.2266(8) Å. [Cu(bdmpab)Br_2] crystallises in space group $P2_1/n$, with a = 8.742(3), b = 29.408(5), c = 8.522(1) Å, β = 107.77(2)°, and Z = 4. Standard least-squares refinement gave R = 0.025 (R' = 0.026). The copper atom has a CuN_3Br_2 chromophore in a distorted trigonal-bipyramidal geometry. The pyrazole nitrogens occupy the axial positions. Cu–N distances are 1.988(5) and 1.981(5) Å for the pyrazole nitrogens and 2.423(1) Å for the aniline nitrogen. Cu–Br distances are 2.454(1) and 2.414(1) Å.

During the last decade the co-ordination chemistry of pyrazole and its derivatives has been the subject of many studies.[1,2] However, with the exception of the poly(pyrazolyl)borates,[3] detailed studies of pyrazole-based ligands, with variables as the steric constraints, the presence of other functional groups, and the number of donor sites available for co-ordination, have not been reported.

Recently a new method for the synthesis of a large variety of *N*-substituted pyrazole derivatives was described.[4] This method not only provides routes to a variety of examples of bioinorganic model systems but also offers the opportunity to incorporate pyrazole chelates in polymers, which may lead to ion-exchange resins of improved selectivity.

The studies on this new series of ligands have been started with research into the co-ordination chemistry of the pyrazole derivatives of simple amines, such as ammonia,[5] aminoethane,[6] and aniline. The insight gained into the nature and properties of these compounds may be a good base for studies of more complex chelating systems.

In this paper the synthesis and chelating properties of the aniline-based derivative, *NN*-bis(3,5-dimethylpyrazol-1-ylmethyl)aminobenzene (bdmpab), are described. To prove the chelating nature of bdmpab and to determine whether or not the aniline nitrogen co-ordinates to the metal ions, crystal-structure determinations of two representative examples, [Co(bdmpab)Cl_2] (**1**) and [Cu(bdmpab)Br_2] (**2**), have been included.

Experimental

Syntheses.—The synthesis of the ligand *NN*-bis(3,5-dimethylpyrazol-1-ylmethyl)aminobenzene was performed by a modification of the method reported by Driessen.[4] *N*-Hydroxymethyl-3,5-dimethylpyrazole (25.23 g, 0.21 mol) was added to a solution of aniline (9.31 g, 0.10 mol) in acetonitrile (300 cm^3), a small excess of *N*-hydroxymethyl-3,5-dimethylpyrazole thus being used. This solution was stirred for 3 d in a closed vessel at room temperature. The solvent was then partially removed on a vacuum rotatory evaporator. After cooling to −20 °C a white product crystallized from the solution which was recrystallized from acetonitrile. The compound obtained was characterized by i.r. and proton n.m.r. spectroscopy. The ^{1}H n.m.r. spectrum (solvent $CDCl_3$, reference $SiMe_4$) showed the following signals: singlets at 2.03 (6 H) and 2.20 (6 H), representing the pyrazole methyl groups, singlets at 5.47 (4 H) and 5.68 (2 H) representing respectively the methylene bridges and the pyrazole hydrogens, and a multiplet centred at 7.0 p.p.m. (5 H) representing the phenyl group.

Except for nickel, copper, and zinc thiocyanate, all other chemicals were commercially available, of sufficient purity, and used without further treatment.

The co-ordination compounds were prepared by dissolving the appropriate hydrated metal salt (5 mmol) in ethanol (25

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† *Supplementary data available* (No. SUP 56248, 8 pp.): H-atom co-ordinates, isotropic and anisotropic thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

cm^3) and adding this solution to a solution of bdmpab [5 mmol, except for the Zn(NO$_3$)$_2$ compound, in which case 10 mmol was used] in ethanol (25 cm^3). For the preparation of the copper *thio*cyanate compound a different procedure was followed: Cu(SCN)$_2$ was synthesized from Cu(NO$_3$)$_2$ (5 mmol) and NH$_4$SCN (10 mmol) as previously reported.[7] The resulting black powder was added to a solution of bdmpab (5 mmol) in methanol (50 cm^3). In the case of nickel and zinc thiocyanate a solution of the metal nitrate or perchlorate (5 mmol) was added to a solution of the ligand (5 mmol), and to the resulting solution a solution of NH$_4$SCN (10 mmol) was added. All the co-ordination compounds appeared to be more or less sensitive towards oxidation. In the case of zinc and nickel thiocyanate no co-ordination compounds could be isolated because of a very rapid oxidation of the ligand. To slow down oxidation the solutions were cooled to 4 °C. Upon standing at this temperature, in some cases, after evaporation of part of the solvent on a rotatory evaporator, solid compounds formed which were collected by filtration and washed with a small portion of absolute ethanol. In the case of nickel and copper nitrate no well defined products could be isolated. In spite of several attempts hitherto, no bdmpab complexes have been synthesized containing non-co-ordinating anions such as tetrafluoroborate or perchlorate.

Crystals used for the structure determinations of [Co(bdmpab)Cl$_2$] **(1)** and [Cu(bdmpab)Br$_2$] **(2)** were grown respectively from a solution in tetrahydrofuran–ethanol (50:50, v/v) and from a solution in methanol–ethanol–acetonitrile (50:25:25, v/v).

Characterization.—Metal analyses were carried out complexometrically using ethylenediaminetetra-acetate as the complexing agent.[8] Carbon, H, and N analyses were performed either by Dr. F. Pascher, Bonn, or by the Microanalytical Service Ltd., Vancouver.

Infrared spectra in the range 4 000—200 cm^{-1} of samples mulled in Nujol between NaCl discs or pelleted in KBr were recorded on a Perkin-Elmer 580 spectrophotometer, equipped with a PE Data Station. Far-i.r. spectra (450—100 cm^{-1}) were recorded as Nujol mulls between polyethylene discs with a polyethylene pellet as reference on a Beckman FIR-720 spectrophotometer. Solid-state electronic spectra (28 000—5 000 cm^{-1}) were recorded on a Beckman DK-2A spectrophotometer fitted with a reflectance attachment, using MgO as reference and on a Perkin-Elmer 330 spectrophotometer, equipped with a PE Data Station.

Electron spin resonance spectra of the powdered copper compounds were obtained with a Varian E-3 spectrophotometer at *X*-band frequencies at room temperature and at 77 K (liquid nitrogen).

X-Ray powder diffraction diagrams of the compounds were obtained with a Guinier-type camera using Cu-K_α radiation. The samples were protected from atmospheric vapour by adhesive tape.

Crystal Data.—**(1)** C$_{18}$H$_{23}$Cl$_2$CoN$_5$, M = 439.25, orthorhombic, space group *Pbca*, a = 8.713(2), b = 17.252(4), c = 27.626(7) Å, U = 4 153 Å^3, Z = 8, D_c = 1.41 g cm^{-3}, $F(000)$ = 1 821, μ(Mo-$K_{\bar{\alpha}}$) = 10.95 cm^{-1}, λ(Mo-$K_{\bar{\alpha}}$) = 0.710 73 Å. **(2)** C$_{18}$H$_{23}$Br$_2$CuN$_5$, M = 532.77, monoclinic, space group $P2_1/n$, a = 8.742(3), b = 29.408(5), c = 8.522(1) Å, β = 107.77(2)°, U = 2 087 Å^3, Z = 4, D_c = 1.69 g cm^{-3}, $F(000)$ = 1 058, μ(Mo-$K_{\bar{\alpha}}$) = 48.24 cm^{-1}, λ(Mo-$K_{\bar{\alpha}}$) = 0.710 73 Å.

Data Collection and Structure Refinement.—A single crystal of approximate dimensions 0.24 × 0.28 × 0.56 mm **(1)** [0.45 × 0.49 × 0.22 mm **(2)**], mounted in a glass capillary, was used for data collection. Cell dimensions were determined by least-squares refinement from the measured setting angles of 24 reflections [$14 < \theta < 15°$ **(1)** and $9 < \theta < 12°$ **(2)**]. *X*-Ray intensities were collected on a four-circle Enraf-Nonius diffractometer at room temperature by the ω/θ scan technique for $2 < \theta < 24°$ with $0 < h < 9, 0 < k < 19$, and $-31 < l < 31$ for **(1)**, and for $2 < \theta < 22°$ with $-9 < h < 9, 0 < k < 31$, and $0 < l < 9$ for **(2)**. The scanning rate was adjusted to the required precision of $\sigma(I)/I = 0.01$, with a maximum scan time of 90 s per reflection. Intensities were corrected for background. The instrument and crystal stability were checked every 5 400 s of radiation time by measuring three reference reflections: no significant changes in the intensities were observed. In total 6 404 **(1)** and 2 828 **(2)** reflections were measured, of which 3 239 **(1)** and 2 624 **(2)** were independent; from these 2 311 **(1)** and 1 482 **(2)** were considered as observed [$I > 2\sigma(I)$]. Because the absorption effect on $I_{\text{obs.}}$ was 24%, a correction was applied in the case of **(2)** with a Monte Carlo method as described by de Graaff.[9] For **(1)**, the effect on $I_{\text{obs.}}$ was only 2.9% and an absorption correction was not necessary. Intensities were corrected for Lorentz and polarization effects. The calculations were performed on the Leiden University Amdahl V7B computer using a local set of computer programs. Scattering factors and anomalous dispersion corrections were taken from ref. 10. The structure was solved by the heavy-atom technique and refined by full-matrix least-squares calculations. Convergence was considered to be reached when the changes in the parameters were smaller than one third of the standard deviation. Hydrogen atoms were located from difference-Fourier maps, and their positional and isotropic thermal parameters were refined also. The thermal parameters of the non-hydrogen atoms were anisotropically refined. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. At the final stage the conventional discrepancy index $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ had been reduced to 0.031 **(1)** and 0.025 **(2)** and the weighted factor $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ to 0.028

Table 1. Fractional co-ordinates [Co, Cl(1), and Cl(2) × 10^5; others × 10^4] for the non-hydrogen atoms of [Co(bdmpab)Cl$_2$] **(1)***

Atom	*X/a*	*Y/b*	*Z/c*
Co	23 184(3)	12 305(2)	13 596(1)
Cl(1)	45 264(9)	17 914(5)	11 319(3)
Cl(2)	25 566(9)	−73(5)	15 749(3)
N(10)	−475(3)	2 906(1)	1 086(1)
C(11)	−1 521(3)	3 537(2)	1 143(1)
C(12)	−1 034(4)	4 275(2)	1 027(1)
C(13)	−1 989(5)	4 898(2)	1 099(1)
C(14)	−3 440(5)	4 799(2)	1 260(1)
C(15)	−3 966(4)	4 070(2)	1 360(1)
C(16)	−3 000(4)	3 439(2)	1 308(1)
C(20)	969(3)	2 963(2)	1 349(1)
N(21)	918(3)	2 630(1)	1 836(1)
N(22)	1 335(3)	1 862(1)	1 900(1)
C(23)	1 005(4)	1 710(2)	2 366(1)
C(24)	364(4)	2 357(2)	2 581(1)
C(25)	323(4)	2 930(2)	2 247(1)
C(26)	1 329(9)	940(3)	2 594(2)
C(27)	−219(8)	3 748(3)	2 292(2)
C(30)	−1 092(4)	2 128(2)	1 042(1)
N(31)	−337(3)	1 687(1)	663(1)
N(32)	984(3)	1 275(1)	752(1)
C(33)	1 351(4)	945(2)	328(1)
C(34)	281(5)	1 150(2)	−17(1)
C(35)	−767(4)	1 619(2)	197(1)
C(36)	2 712(6)	440(3)	278(2)
C(37)	−2 171(8)	2 012(4)	1(2)

* Estimated standard deviations in the least significant digits are given in parentheses here and in Tables 2—4.

Table 2. Bond distances (Å) and angles (°) for [Co(bdmpab)Cl$_2$] (**1**)

Co–Cl(1)	2.2434(8)	N(21)–C(25)	1.351(3)
Co–Cl(2)	2.2266(8)	N(22)–C(23)	1.344(3)
Co–N(22)	2.038(2)	C(23)–C(24)	1.382(4)
Co–N(32)	2.044(2)	C(23)–C(26)	1.498(5)
N(10)–C(11)	1.428(3)	C(24)–C(25)	1.355(4)
N(10)–C(20)	1.457(3)	C(25)–C(27)	1.492(5)
N(10)–C(30)	1.451(3)	C(30)–N(31)	1.452(4)
C(11)–C(12)	1.381(4)	N(31)–N(32)	1.375(3)
C(11)–C(16)	1.376(4)	N(31)–C(35)	1.345(4)
C(12)–C(13)	1.374(4)	N(32)–C(33)	1.340(4)
C(13)–C(14)	1.351(5)	C(33)–C(34)	1.379(4)
C(14)–C(15)	1.367(5)	C(33)–C(36)	1.478(5)
C(15)–C(16)	1.384(4)	C(34)–C(35)	1.356(5)
C(20)–N(21)	1.462(3)	C(35)–C(37)	1.499(6)
N(21)–N(22)	1.385(3)		

Cl(1)–Co–Cl(2)	114.12(3)	N(10)–C(20)–N(21)	113.9(2)
Cl(1)–Co–N(22)	109.60(7)	C(20)–N(21)–N(22)	119.1(2)
Cl(1)–Co–N(32)	103.96(7)	C(20)–N(21)–C(25)	129.3(3)
Cl(2)–Co–N(22)	110.86(7)	N(22)–N(21)–C(25)	111.0(2)
Cl(2)–Co–N(32)	107.96(7)	N(21)–N(22)–C(23)	104.7(2)
N(22)–Co–N(32)	110.08(9)	N(22)–C(23)–C(24)	109.9(3)
Co–N(22)–N(21)	121.8(2)	N(22)–C(23)–C(26)	122.3(4)
Co–N(22)–C(23)	133.4(2)	C(24)–C(23)–C(26)	127.7(3)
Co–N(32)–N(31)	129.9(2)	C(23)–C(24)–C(25)	107.9(3)
Co–N(32)–C(33)	124.5(2)	C(24)–C(25)–C(27)	129.9(4)
C(11)–N(10)–C(20)	116.4(2)	N(21)–C(25)–C(27)	123.6(3)
C(11)–N(10)–C(30)	118.5(2)	N(21)–C(25)–C(24)	106.4(3)
C(20)–N(10)–C(30)	115.1(2)		
N(10)–C(11)–C(12)	118.7(3)	N(10)–C(30)–N(31)	112.2(3)
N(10)–C(11)–C(16)	122.7(3)	C(20)–N(31)–N(32)	121.4(2)
C(12)–C(11)–C(16)	118.5(3)	C(30)–N(31)–C(35)	127.5(3)
C(11)–C(12)–C(13)	120.1(3)	N(32)–N(31)–C(35)	111.0(3)
C(12)–C(13)–C(14)	121.0(4)	N(31)–N(32)–C(33)	105.3(2)
C(13)–C(14)–C(15)	119.8(4)	N(32)–C(33)–C(34)	109.4(3)
C(14)–C(15)–C(16)	119.9(4)	N(32)–C(33)–C(36)	121.6(4)
C(11)–C(16)–C(15)	120.5(3)	C(34)–C(33)–C(36)	129.0(4)
		C(33)–C(34)–C(35)	107.9(3)
		C(34)–C(35)–C(37)	131.4(4)
		N(31)–C(35)–C(37)	122.2(4)
		N(31)–C(35)–C(34)	106.3(3)

(**1**) and 0.026 (**2**). Non-hydrogen atomic co-ordinates are listed in Table 1 (**1**) and Table 3 (**2**). Non-hydrogen bond distances and angles are given in Table 2 (**1**) and Table 4 (**2**).

Results and Discussion

General.—Analytical data, *X*-ray powder diffraction types, and melting points of the new complexes are given in Table 5. In Tables 6, 7, and 8 i.r. spectroscopic data, ligand-field absorption bands, *X*-band e.s.r. data, and far-i.r. spectroscopic data are listed. Many details in the i.r. spectra of the complexes are characteristic of pyrazole derivatives.[11,12] Assignment of some of the metal–nitrogen stretching vibrations is based on earlier work.[2,5] Isomorphism is found for [Co(bdmpab)Cl$_2$] and [Zn(bdmpab)Cl$_2$] and for [Co(bdmpab)Br$_2$] and one of the two [Zn(bdmpab)Br$_2$] compounds, but not for the corresponding chloride and bromide compounds. However, the spectral and analytical data indicate that the cobalt and zinc halide compounds all have very similar co-ordination geometries. Likewise [Cu(bdmpab)Cl$_2$] and [Cu(bdmpab)Br$_2$], although not completely isomorphous according to line intensities and positions in the *X*-ray diffractograms, have very similar co-ordination geometries.

To obtain information about the precise co-ordination modes of bdmpab and to understand the spectroscopic data the *X*-ray crystal structures of [Co(bdmpab)Cl$_2$] (**1**) and [Cu(bdmpab)Br$_2$] (**2**) have been determined. From a combination of the structural and i.r. data it is found that the pattern of the i.r. absorption bands in the region 900—1 000 cm^{-1} indicates whether or not the aniline nitrogen co-ordinates to the metal ion. When the aniline nitrogen does not co-ordinate, as in [Co(bdmpab)Cl$_2$], a band of medium intensity is visible between 920 and 935 cm^{-1}. But when the aniline nitrogen co-ordinates, as in [Cu(bdmpab)Br$_2$], this band is positioned at *ca.* 975 cm^{-1} (see Table 8).

Table 3. Fractional co-ordinates [Cu, Br(1), and Br(2) × 10^5; others × 10^4] for the non-hydrogen atoms of [Cu(bdmpab)Br$_2$] (**2**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	26 730(8)	9 351(2)	6 745(8)
Br(1)	5 224(8)	14 442(3)	8 897(9)
Br(2)	25 851(9)	1 835(2)	−4 894(8)
N(10)	5 446(5)	1 178(2)	1 761(5)
C(11)	5 851(7)	1 625(2)	2 501(6)
C(12)	7 418(8)	1 786(3)	2 916(8)
C(13)	7 783(10)	2 206(3)	3 606(10)
C(14)	6 622(11)	2 479(3)	3 887(10)
C(15)	5 096(10)	2 321(3)	3 473(9)
C(16)	4 692(9)	1 895(2)	2 791(8)
C(20)	5 836(8)	1 124(2)	217(7)
N(21)	4 611(5)	1 362(2)	−1 051(6)
N(22)	3 044(5)	1 238(2)	−1 262(6)
C(23)	2 199(7)	1 435(2)	−2 656(8)
C(24)	3 192(8)	1 681(2)	−3 352(8)
C(25)	4 721(8)	1 630(2)	−2 307(7)
C(26)	448(11)	1 363(5)	−3 333(15)
C(27)	6 279(13)	1 832(5)	−2 327(18)
C(30)	6 016(8)	805(2)	2 914(9)
N(31)	4 878(7)	740(2)	3 828(6)
N(32)	3 277(6)	714(2)	2 978(6)
C(33)	2 561(9)	570(2)	4 068(10)
C(34)	3 698(11)	496(2)	5 567(10)
C(35)	5 160(10)	604(2)	5 414(8)
C(36)	802(13)	501(5)	3 576(16)
C(37)	6 776(13)	583(3)	6 618(11)

With some metal salts only a decomposition product of bdmpab was obtained. The formation and crystal structure of a decomposition product containing the monodentate ligand 3,5-dimethylpyrazole (abbreviated dmpz) with the composition Zn(bdmpab)(dmpz)(NO$_3$)$_2$ will be described elsewhere.[13] With nickel chloride and bromide a cluster compound containing deprotonated *N*-hydroxymethyl-3,5-dimethylpyrazole (HL) was obtained. This compound, with the composition [Ni$_4$X$_4$(L)$_4$(C$_2$H$_5$OH)$_4$] (X = Cl or Br), has already been described in earlier work.[14]

Description of the Structure of [Co(bdmpab)Cl$_2$] (**1**) *and* [Cu(bdmpab)Br$_2$].—In (**1**) the cobalt ion is surrounded by the two pyrazole nitrogens and the two chloride ions in a slightly distorted tetrahedral configuration (see Figure 1). The ligand bdmpab utilizes only two of the three *N*-donor sites for co-ordination thereby acting as a bidentate ligand. The distance between the cobalt ion and the aniline nitrogen is 3.854(2) Å. Instead of co-ordinating, the lone pair on the nitrogen atom conjugates to the aromatic system of the phenyl ring as can be seen from the angles around the aniline nitrogen which lie close to 120° (see Table 2). The cobalt to pyrazole-nitrogen distances are normal for this kind of compound.[5,6,15] Also the angles between the co-ordination bonds do not deviate much from the ideal tetrahedral angles (Table 2).

In (**2**) the copper ion is surrounded by three nitrogens and

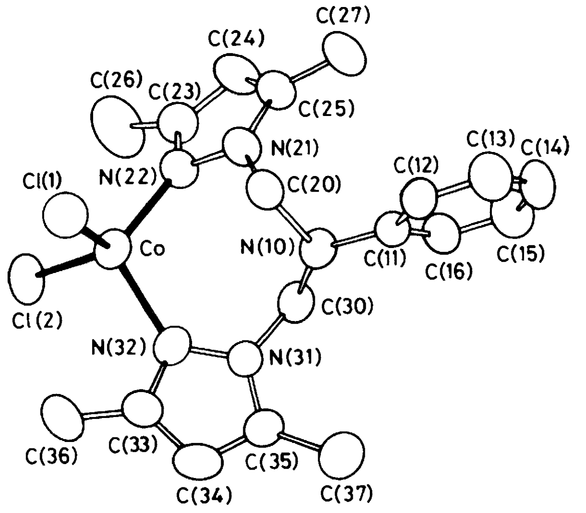

Figure 1. ORTEP projection of [Co(bdmpab)Cl$_2$] (1), hydrogen atoms are omitted

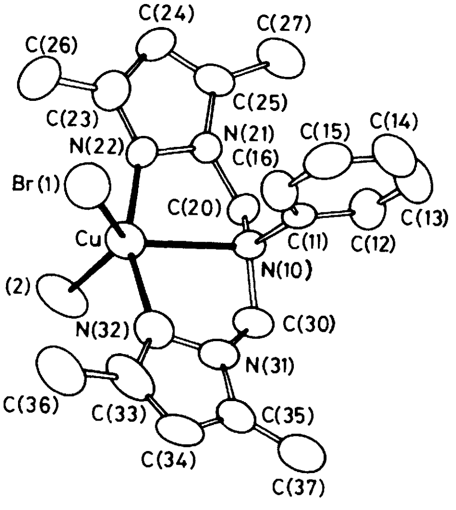

Figure 2. ORTEP projection of [Cu(bdmpab)Br$_2$] (2), hydrogen atoms are omitted

Table 4. Bond distances (Å) and angles (°) for [Cu(bdmpab)Br$_2$] (2)

Cu–Br(1)	2.454(1)	N(21)–C(25)	1.357(6)
Cu–Br(2)	2.414(1)	N(22)–C(23)	1.325(7)
Cu–N(10)	2.423(1)	C(23)–C(24)	1.394(8)
Cu–N(22)	1.988(5)	C(23)–C(26)	1.478(10)
Cu–N(32)	1.981(5)	C(24)–C(25)	1.369(8)
N(10)–C(11)	1.456(7)	C(25)–C(27)	1.489(11)
C(11)–C(12)	1.389(8)	N(10)–C(30)	1.456(7)
C(11)–C(16)	1.367(8)	C(30)–N(31)	1.451(7)
C(12)–C(13)	1.363(9)	N(31)–N(32)	1.368(6)
C(13)–C(14)	1.371(10)	N(31)–C(35)	1.357(7)
C(14)–C(15)	1.354(10)	N(32)–C(33)	1.337(7)
C(15)–C(16)	1.381(9)	C(33)–C(34)	1.376(9)
N(10)–C(20)	1.465(7)	C(33)–C(36)	1.480(12)
C(20)–N(21)	1.449(7)	C(34)–C(35)	1.362(9)
N(21)–N(22)	1.375(5)	C(35)–C(37)	1.472(11)
Br(1)–Cu–Br(2)	131.32(4)	N(21)–C(25)–C(27)	121.7(7)
Br(1)–Cu–N(10)	119.5(1)	N(21)–C(25)–C(24)	106.6(6)
Br(1)–Cu–N(22)	96.4(1)	N(10)–C(20)–N(21)	107.2(5)
Br(1)–Cu–N(32)	96.0(1)	C(20)–N(21)–N(22)	116.7(5)
Br(2)–Cu–N(10)	109.2(1)	C(20)–N(21)–C(25)	131.0(5)
Br(2)–Cu–N(22)	93.6(1)	N(22)–N(21)–C(25)	111.0(5)
Br(2)–Cu–N(32)	94.1(1)	N(21)–N(22)–C(23)	105.2(4)
N(10)–Cu–N(22)	77.7(2)	N(22)–C(23)–C(24)	111.0(5)
N(10)–Cu–N(32)	77.6(2)	N(22)–C(23)–C(26)	121.0(7)
N(22)–Cu–N(32)	155.3(2)	C(24)–C(23)–C(26)	127.9(8)
Cu–N(10)–C(11)	121.0(3)	C(23)–C(24)–C(25)	106.2(6)
Cu–N(10)–C(20)	96.0(3)	C(24)–C(25)–C(27)	131.6(7)
Cu–N(10)–C(30)	97.6(4)		
Cu–N(22)–N(21)	114.7(4)	N(10)–C(30)–N(31)	108.2(5)
Cu–N(22)–C(23)	138.8(4)	C(30)–N(31)–N(32)	118.8(5)
Cu–N(32)–N(31)	115.2(4)	C(30)–N(31)–C(35)	128.8(6)
Cu–N(32)–C(33)	138.8(5)	N(32)–N(31)–C(35)	110.9(5)
		N(31)–N(32)–C(33)	105.7(5)
C(11)–N(10)–C(20)	113.2(5)	N(32)–C(33)–C(34)	109.7(6)
C(11)–N(10)–C(30)	113.7(5)	N(32)–C(33)–C(36)	120.9(8)
C(20)–N(10)–C(30)	113.5(5)	C(34)–C(33)–C(36)	129.4(7)
N(10)–C(11)–C(16)	120.5(6)	C(33)–C(34)–C(35)	107.9(6)
N(10)–C(11)–C(12)	120.6(6)	C(34)–C(35)–C(37)	130.7(7)
C(12)–C(11)–C(16)	110.0(6)	N(31)–C(35)–C(37)	123.4(7)
C(11)–C(12)–C(13)	120.0(7)	N(31)–C(35)–C(34)	105.8(7)
C(12)–C(13)–C(14)	121.2(8)		
C(13)–C(14)–C(15)	118.4(8)		
C(14)–C(15)–C(16)	121.7(8)		
C(11)–C(16)–C(15)	119.6(7)		

two bromide ions in a configuration which can be described as distorted trigonal bipyramidal (see Figure 2). The ligand bdmpab now utilizes all its *N*-donor sites for co-ordination and acts as a tridentate ligand. The pyrazole nitrogens occur as axial ligands. The aniline nitrogen and the bromide ions occupy equatorial positions with the distance of the copper ion to the least-squares plane being less than 0.002 Å. The distance between the aniline nitrogen and the copper ion is 2.423(1) Å. Hence the lone pair on the aniline nitrogen co-ordinates to Cu and is no longer available for conjugation to the aromatic system of the phenyl ring. In accordance the angles around the aniline nitrogen do not diverge greatly from the ideal tetrahedral angles (see Table 4). All the co-ordination bond lengths are normal for this kind of compound. The N(10)–Cu–N(22) and N(10)–Cu–N(32) angles are *ca.* 80° and deviate significantly from the ideal co-ordination angle of *ca.* 90°. Also the angles which the Cu–N(22) and the Cu–N(32) bonds make with N(22)–C(23) and N(32)–C(33) and with N(22)–N(21) and N(32)–N(31), respectively *ca.* 139 and 115°, deviate significantly from the ideal angles of *ca.* 125°. Apparently the geometry of the ligand is not very well suited for regular trigonal-bipyramidal co-ordination of the copper ion, leading to an adjustment of the co-ordination angles. This phenomenon was also found with related ligands.[5,6]

Comparing the structures of (**1**) and (**2**) it is obvious that bdmpab is a flexible ligand. Because of this flexibility its co-ordination mode strongly depends on the preference of the metal ions for specific co-ordination geometries. In (**1**) the cobalt ion has a common tetrahedral co-ordination. In (**2**) the copper ion does not fit into such a tetrahedral co-ordination, whereas a square-planar structure is unfavourable for sterical reasons. Owing to this and to the fact that the bulky ligand hinders the co-ordination of an additional ligand it becomes possible for the aniline nitrogen to lose conjugation in exchange for co-ordination to the copper ion. In both (**1**) and in (**2**), the pyrazole rings are planar and the methyl carbons are coplanar with the respective pyrazole rings (distances to the least-squares planes less than 0.08 Å). In both structures the pyrazole rings are neither coplanar with the phenyl ring nor mutually coplanar. In both compounds no stacking between the aromatic rings occurs. The packing of the molecular units proceeds *via* normal van der Waals contacts.

Table 5. Analytical data, X-ray powder diffraction type, and melting points of complexes with bdmpab

Compound	Colour	Analysis[a] (%) M	C	H	N	M.p.[b] (°C)	X-Ray[c] type
[Co(bdmpab)Cl_2]	Dark blue	13.30 (13.40)	49.20 (49.20)	5.35 (5.30)	15.95 (15.95)	169—170	A
[Co(bdmpab)Br_2]	Dark blue	11.00 (11.15)	— (40.95)	— (4.40)	— (13.25)	153—154	B
[Co(bdmpab)$(SCN)_2$]	Blue-purple	12.30 (12.15)	48.80 (49.60)	4.75 (4.80)	20.20 (20.25)	168—169	—
[Co(bdmpab)$(NO_3)_2$]	Red	11.85 (11.95)	43.85 (43.90)	4.65 (4.70)	19.75 (19.90)	176—177	—
[Zn(bdmpab)Cl_2]	White	14.50 (14.65)	48.40 (48.50)	5.25 (5.20)	15.70 (15.70)	164—165	A
[Zn(bdmpab)Br_2][d]	White	12.25 (12.25)	40.45 (40.45)	4.50 (4.35)	13.25 (13.10)	151—152	—
[Zn(bdmpab)Br_2][d]	White	12.15 (12.25)	40.00 (40.45)	4.50 (4.35)	13.15 (13.10)	151—152	B
[Cu(bdmpab)Cl_2]	Light green	14.20 (14.30)	— (48.70)	— (5.20)	— (15.80)	140—141	—
[Cu(bdmpab)Br_2]	Orange-brown	11.85 (11.95)	40.95 (40.60)	4.55 (4.35)	13.10 (13.15)	129—130	—
[Cu_2(bdmpab)$(SCN)_3$][e]	Blackish green	— (20.80)	41.80 (41.30)	4.25 (3.80)	18.55 (18.35)	117—118	—

[a] Calculated values in parentheses. [b] Decomposition temperature. [c] Very similar line pattern and intensities in powder diagrams. [d] See text. [e] %S: found 15.50, calc. 15.75.

Table 6. Ligand-field absorption bands (cm^{-1}) and X-band e.s.r. spectral data

[Co(bdmpab)Cl_2]	6 100, 7 500, 9 100, 16 500	
[Co(bdmpab)Br_2]	6 000, 7 000, 8 600, 15 100, 16 000, 16 900, 18 800(sh), 22 400(sh), 23 400(sh)	
[Co(bdmpab)$(SCN)_2$]	5 500(sh), 6 800(sh), 7 600, 10 100(sh), 11 800(sh), 17 400	
[Co(bdmpab)$(NO_3)_2$]	7 300, 7 700, 9 700, 13 100, 19 200	
[Cu(bdmpab)Cl_2]	9 500—11 500,[a] 27 400	$g_1 = 2.27, g_2 = 2.15, g_3 = 2.02$
[Cu(bdmpab)Br_2]	9 500—11 500,[a] 22 700	$g_1 = 2.24, g_2 = 2.13, g_3 = 2.03$
[Cu_2(bdmpab)$(SCN)_3$]	13 500, 27 000	$g_{\parallel} = 2.22, g_{\perp} = 2.08, A_{\parallel} = 125$ G[b]

[a] Broad maximum from 9 500 to 11 500 cm^{-1}. [b] G = 10^{-4} T.

Table 7. Infrared spectral data of the thiocyanate and nitrate compounds

Compound	Vibrations/cm^{-1}
[Co(bdmpab)$(SCN)_2$]	ν[CN(SCN)] 2 051, 2 079
[Cu_2(bdmpab)$(SCN)_3$]	ν[CN(SCN)] 2 081(sh), 2 093, 2 112
[Co(bdmpab)$(NO_3)_2$]	$\nu_1 + \nu_4$ (NO_3) 1 715, 1 729, 1 737, 1 757

Cobalt and Zinc Halide Compounds.—The spectral properties of [Co(bdmpab)Cl_2] (**1**) are consistent with the X-ray structure description given above. The ligand-field spectrum is typical for high-spin cobalt(II) in a (distorted) tetrahedral configuration (see Table 6).[16] The far-i.r. spectrum shows bands at 334 and 307 cm^{-1} (Table 8), which are in agreement with asymmetric and symmetric Co–Cl stretching vibrations in tetrahedral four-co-ordinate cobalt(II) chloride compounds.[17,18] X-Ray powder diffraction data show that [Co(bdmpab)Cl_2] and [Zn(bdmpab)Cl_2] are isomorphous (Table 5) (*i.e.* have similar line positions and intensities). The far-i.r. spectrum of [Zn(bdmpab)Cl_2] shows bands at 324 and 294 cm^{-1}. These values are in good agreement with Zn–Cl vibrations in a four-co-ordinate zinc chloride compound.[17–19] Evidence for the non-co-ordination of the aniline nitrogen in [Zn(bdmpab)Cl_2] comes from the presence of a band of medium intensity at 932 cm^{-1} (see Table 8).

The cobalt- and zinc-bromide compounds have the same stoicheiometry as the chloride analogues. The spectral data indicate that these bromides also have tetrahedral four-co-ordination of the metal ion, the aniline nitrogen not being co-ordinated (bands of medium intensity between 920 and 935 cm^{-1}; see Table 8). However, the chlorides and bromides of the same metal ion are not X-ray isomorphous. In the case of [Zn(bdmpab)Br_2] even two different products with the same stoicheiometry and analyses were isolated (Table 5). Their i.r. spectra only differ in small details, not large enough to originate from a different structure. It is most likely that they only differ in the packing between the molecules in the lattice. The same synthetic method was used in both cases.

The ligand-field spectrum of [Co(bdmpab)Br_2] is typical for high-spin cobalt(II) in a distorted tetrahedral environment.[16]

Copper Halide Compounds.—A description of the crystal structure of [Cu(bdmpab)Br_2] (**2**) has been given above. The chloride derivative has the same stoicheiometry (Table 5). The two compounds are not powder isomorphous, but from the spectral data, which are very similar, it is clear that they have the same co-ordination geometry. E.s.r. measurements on both compounds reveal three g values with the lowest g value being 2.02 and 2.03 respectively for the chloride and bromide (Table 6). This can be interpreted in terms of a distorted trigonal

Table 8. Infrared and far-i.r. spectral data of the compounds with bdmpab (frequencies in cm^{-1})

Compound	Medium band in the region 900—1 000 cm^{-1}	Absorptions in the far-i.r. region[a]
bdmpab	—	469s, 451s, 418w, 402m, 373m, 349(sh), 341m, 297m, 269m, 237m, 210m, 194m, 164m
[Co(bdmpab)Cl$_2$]	932	495m, 482s, 464s, 430w, 412m, 388m, 358(sh), *334br*, 317(sh), *307vs br*, 260m, 224s, 200(sh), 184s, 122s
[Zn(bdmpab)Cl$_2$]	932	481s, 464s, 412m, 389m, 358(sh), 349m, *324vs br*, *294vs br*, 261m, 202m, 180s, 122s
[Cu(bdmpab)Cl$_2$]	975	458m, 432s, 362w, 347s, 314m, *290vs br*, **238vs**, 214vs, 142vs, 123m
[Co(bdmpab)Br$_2$]	923	492m, 458m, 434m, 408w, 396m, 368m, 354s, 340m, 314m, 300s, 278s, *263vs*, *242s*, 230m, 198m, 186w
[Zn(bdmpab)Br$_2$][b]	933	491m, 459w, 430w, 409w, 395m, 358s, 340m, 317m, 298s, 262s, *246vs*, *219vs*, 202s, 175s
[Zn(bdmpab)Br$_2$][b]	923	492m, 458m, 434w, 410w, 397m, 369m, 355s, 339m, 313w, 298s, 273s, *246vs*, *220vs*, 194m, 185m
[Cu(bdmpab)Br$_2$]	974	459m, 434s, 370w, 352w, 318m, 294m, **243vs br**, *224s*, 202s, 155s, 134m, 120m
[Co(bdmpab)(SCN)$_2$]	947	
[Cu$_2$(bdmpab)(SCN)$_3$]	975	
[Co(bdmpab)(NO$_3$)$_2$]	953	

[a] Frequencies given in italic type are tentatively assigned to metal–anion stretching vibrations and frequencies given in bold type are tentatively assigned to metal–nitrogen stretching vibrations. [b] See text.

bipyramidal structure having a d_{z^2} ground state.[20] Diffuse-reflectance spectra of both compounds show a broad band centered at *ca.* 10 500 cm^{-1}. This is not unusual for this geometry around the copper ion, although sometimes a high-energy shoulder is observed.[20,21] In the 900—1 000 cm^{-1} region of both compounds a medium band is present at *ca.* 975 cm^{-1} (see Table 8), indicating co-ordination of the aniline nitrogen to the copper ion (see above).

Nitrates and Thiocyanates.—As has been mentioned above only a limited number of nitrate and thiocyanate compounds could be isolated. The composition of the cobalt thiocyanate compound is [Co(bdmpab)(SCN)$_2$]. Although the ligand-field spectrum of [Co(bdmpab)(SCN)$_2$] is not typical for cobalt(II) in a tetrahedral environment, it resembles the spectrum of some known tetrahedral cobalt(II) compounds (Table 6).[22,23] In the 900—1 000 cm^{-1} region a band of medium intensity is located at 947 cm^{-1} (Table 8). This is between 932 cm^{-1} as found for [Co(bdmpab)Cl$_2$] with a non-co-ordinating aniline nitrogen and 974 cm^{-1} as found for [Cu(bdmpab)Br$_2$] with a relatively weakly co-ordinating aniline nitrogen. Therefore in [Co(bdmpab)(SCN)$_2$] bidentate co-ordination by bdmpab is most likely. CN stretching absorptions at 2 051 and 2 079 cm^{-1} are consistent with the presence of two *N*-bonded thiocyanates (Table 7).[24] Because of the occurrence of ligand bands in the same region of the i.r. spectrum assignments of absorptions to other thiocyanato-vibrations cannot be made.

The copper thiocyanate compound, which is a mixed copper(II)–copper(I) species, has the composition [Cu$_2$(bdmpab)(SCN)$_3$]. The stereochemistry of this complex cannot be deduced fully from the data presented here. In the i.r. spectrum CN stretching absorptions suggest the presence of two different NCS species: either one monodentate *N*-bonded and one bridging bidentate or two differently bridging bidentates (Table 7).[24] From the position of the i.r. band in the region of 900—1 000 cm^{-1} it is concluded that the aniline nitrogen takes part in co-ordination. The main absorption band at 13 500 cm^{-1} indicates a five- or a six-co-ordinate copper(II) geometry. The e.s.r. spectrum is axial with $g_\perp = 2.08, g_\parallel = 2.22$, and $A_\parallel = 125$G. Full characterization of this compound, however, must await a crystal-structure determination.

The compound [Co(bdmpab)(NO$_3$)$_2$] exhibits a rather complicated ligand-field spectrum. It resembles the ligand-field spectrum of a related compound. [Co(bdmpae)(NO$_3$)$_2$] [bdmpae = *NN*-bis(3,5-dimethylpyrazol-1-ylmethyl)aminoethane],[6] for which a structure in between square pyramidal and distorted octahedral, with the tertiary amine nitrogen in semi-co-ordination, has been proposed. The i.r. spectrum of [Co(bdmpab)(NO$_3$)$_2$] is not very helpful with respect to nitrate co-ordination since many ligand bands appear in the same region as the nitrate absorptions. However, combination bands are indicative of the presence of either one monodentate and one bidentate or two monodentate bonded nitrates (Table 7).[25] The band in the 900—1 000 cm^{-1} region is located at 953 cm^{-1}, which suggests that the aniline nitrogen hardly, if at all, takes part in co-ordination (see above). Combining these results we may conclude that a (distorted) five-co-ordinate structure is most likely.

Nickel Compounds.—Despite many attempts no nickel complexes of bdmpab have been isolated. In this connection we note that several nickel complexes of the related ligand bdmpae have been described in earlier work.[6] It appears that the special character of the aniline nitrogen is responsible for the fact that the solid nickel bdmpab complexes are not stable enough to crystallize. In the free ligand the lone pair on the aniline nitrogen conjugates to the aromatic system of the phenyl ring. In the co-ordination compounds the aniline nitrogen does not co-ordinate to the metal ion, unless the energy decrease caused by co-ordination is larger than the energy increase caused by loss of conjugation. The nickel ion shows a strong preference for a six-co-ordinate geometry. However, for the compound [Ni(bdmpae)Cl$_2$] it has been proposed[6] that the nickel is surrounded by five donor atoms only, including the amine nitrogen of the ligand bdmpae. It is possible that in [Ni(bdmpab)Cl_2], bdmpab does not allow a similar structure because the decrease in energy, caused by co-ordination of the aniline nitrogen, is not large enough to accomplish the loss of conjugation.

Conclusions

The present study has shown that interesting co-ordination compounds can be obtained with the new ligand *NN*-bis(3,5-dimethylpyrazol-1-ylmethyl)aminobenzene. In some complexes this pyrazole derivative acts as a tridentate ligand, co-ordinating through both pyrazole nitrogens and through the aniline nitrogen. In other complexes it acts as a bidentate ligand and only co-ordinates through both pyrazole nitrogens. In the latter case the aniline nitrogen participates in the conjugation of the aromatic system of the phenyl ring. Because of this flexible character of the ligand the preference of the transition-metal ions for specific co-ordination geometries is shown by the synthesized co-ordination compounds.

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