Transition-metal Co-ordination Compounds containing a Novel Tridentate Pyrazole Chelating Ligand. *X*-Ray Crystal Structure † of [*NN*-Bis(3,5-dimethylpyrazol-1-ylmethyl)aminoethane](nitrato-*O*)-(nitrato-*O,O'*)nickel(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)aminoethane (bdmpae) are described. The compounds have the general formulae [M(bdmpae)X_2] (M = Co, Ni, Cu, or Zn; X = Cl, Br, or NO_3) and $[M(bdmpae)_2][ClO_4]_2$ (M = Co or Ni). The compounds have been characterized by spectroscopic measurements and conductivity studies in solution. In most compounds the ligand behaves as a chelating tridentate ligand. In the mono-adducts the co-ordination around the metal ions is completed by two anions, resulting in a five-co-ordinate geometry (X = Cl or Br) or a six-co-ordinate geometry (X = NO_3; in this case one nitrate is monodentate and the other is bidentate). The bis-adducts appear to have distorted octahedral co-ordination geometries for the metal ions. To prove the chelating nature of the ligand, and in particular the co-ordination of the amine nitrogen, the *X*-ray structure of one representative example was undertaken. Crystals of $[Ni(bdmpae)(NO_3)_2]$ are of space group $P2_1/c$, with $a = 8.511(3)$, $b = 14.103(3)$, $c = 15.865(8)$ Å, $\beta = 92.75(3)°$, and $Z = 4$. Standard least-squares refinements resulted in $R = 0.041$ ($R' = 0.059$). The nickel atom has a NiN_3O_3 (*mer*) chromophore in a distorted octahedral geometry. One nitrate group is monodentate [Ni–O 2.052(5) Å], whereas the other is bidentate [Ni–O 2.157(5) and 2.145(5) Å]. Ni–N distances are 2.061(5) and 2.034(5) Å for the pyrazole nitrogens and 2.128(5) Å for the amine nitrogen.

The co-ordination chemistry of pyrazole and its derivatives has received much attention during the last few years.[1,2] The variety in pyrazole chelates is neither very large nor systematic, with the exception of poly(pyrazolyl)borates.[3] However, recently we reported a novel method for the synthesis of *N*-substituted pyrazole chelates,[4] through which a large systematic variety of pyrazole derivatives can be obtained. This method provides routes to a variety of examples of bioinorganic model systems and also offers the opportunity to incorporate pyrazole chelates into polymers. Most known chelating polymers do not differentiate to a large enough extent between transition-metal ions on the one hand and alkali and alkaline-earth ions, notably Mg^{2+} and Ca^{2+}, on the other.[5,6] It is expected that the differentiation will be better with chelating polymers containing heterocyclic N-donors as the active sites. As a first approach to tackle these problems one of the simplest pyrazole derivatives obtained with our new method,[4] *viz.* *NN*-bis(3,5-dimethylpyrazol-1-ylmethyl)aminoethane (bdmpae), has been chosen for co-ordination chemistry studies. In this paper we present the results obtained with a variety of divalent first-row transition-metal salts. To prove the chelating nature of bdmpae and to see whether or not the central, tertiary amine co-ordinates to the metal ions, a crystal structure determination of a representative example has been included.

Experimental

The ligand *NN*-bis(3,5-dimethylpyrazol-1-ylmethyl)aminoethane was synthesized following the procedure described by Driessen:[4] *N*-hydroxymethyl-3,5-dimethylpyrazole (0.50 mol) was added to a solution of aminoethane (0.25 mol) in dichloromethane (50 cm^3). This solution was stirred for 24 h in a closed vessel at room temperature. The dichloromethane layer was then separated from the water layer and the organic solvent was removed on a vacuum rotatory evaporator, yielding a light yellowish product, which was characterized by i.r. and ^{1}H n.m.r. spectroscopy. The ^{1}H n.m.r. spectrum (solvent $CDCl_3$, reference $SiMe_4$) showed the following signals (relative intensities in parentheses): 2.66 (q, 18) and 1.01 p.p.m. (t, 29), due to the ethyl group; 2.16 p.p.m. (s, 135), due to the pyrazole methyl groups; 4.82 (s, 42) and 5.72 p.p.m. (s, 25), due respectively to the methylene bridges and the pyrazole hydrogens.

The commercially available hydrated metal salts were of sufficient purity and used without further treatment.

The compounds [M(bdmpae)X_2] (M = Co^{II}, Ni^{II}, Cu^{II}, or Zn^{II}; X = Cl, Br, or NO_3) were prepared by dissolving the hydrated metal salts (5 mmol) in absolute ethanol (25 cm^3) and treating them with triethyl orthoformate (4 cm^3) to remove the water; then to each of these solutions a solution of the ligand (5 mmol) in absolute ethanol (25 cm^3) was added. The compounds $[M(bdmpae)_2][ClO_4]_2$ (M = Co^{II} or Ni^{II}) were prepared by dissolving the appropriate hydrated metal salt (5 mmol) in a mixture of absolute ethanol (25 cm^3) and triethyl orthoformate (4 cm^3), and adding each of these solutions to a solution of the ligand (15 mmol) in absolute ethanol (25 cm^3). All compounds crystallized upon standing at room temperature. The crystals were collected on a glass filter, washed with a small portion of absolute ethanol and several portions of sodium-dried diethyl ether and finally dried *in vacuo* at 80 °C. Metal analyses were carried out complexometrically using ethylenediaminetetra-acetate as the complexing agent.[7] Carbon, H, and N analyses were performed either by Dr. F. Pascher, Bonn, or by P. van den Bosch, Eindhoven University of Technology.

Infrared spectra in the range 4 000—200 cm^{-1} of samples mulled in Nujol between KRS-5 discs or as KBr pellets, and far-i.r. spectra in the range 400—200 cm^{-1} of samples as

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† *Supplementary data available* (No. SUP 23877, 11 pp.): H-atom co-ordinates, thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Fractional co-ordinates ($\times 10^5$ for Ni, others $\times 10^4$) for [Ni(bdmpae)(NO_3)$_2$] with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ni	25 796(9)	23 801(6)	4 354(4)	N(22)	4 652(6)	3 041(4)	232(3)
N(02)	2 600(6)	2 196(3)	−895(3)	C(23)	5 682(8)	2 625(5)	576(4)
C(03)	1 632(9)	2 933(5)	−1 382(4)	C(24)	6 795(10)	3 873(6)	−6(5)
C(04)	2 322(11)	3 887(6)	−1 395(5)	C(25)	6 409(7)	3 391(5)	−716(4)
C(10)	1 888(8)	1 279(5)	−1 029(4)	C(26)	5 509(13)	3 962(8)	1 466(6)
N(11)	452(6)	1 255(4)	−559(3)	C(27)	7 180(10)	3 358(7)	−1 545(5)
N(12)	531(6)	1 619(4)	230(3)	N(30)	4 507(6)	1 007(4)	1 306(3)
C(13)	−894(8)	1 477(5)	520(4)	O(31)	3 770(6)	1 123(3)	598(3)
C(14)	−1 837(9)	1 039(5)	−87(4)	O(32)	4 466(8)	1 607(4)	1 837(3)
C(15)	−973(7)	904(5)	−765(4)	O(33)	5 286(6)	249(4)	1 405(4)
C(16)	−1 301(10)	1 811(8)	1 382(5)	N(40)	1 353(8)	3 705(5)	1 295(4)
C(17)	−1 373(10)	466(7)	−1 608(5)	O(41)	1 286(6)	3 691(3)	498(3)
C(20)	4 269(7)	2 190(5)	−1 103(4)	O(42)	2 047(6)	2 995(4)	1 625(3)
N(21)	5 113(6)	2 897(4)	−578(3)	O(43)	788(9)	4 319(5)	1 693(4)

powdered polyethylene pellets with a polyethylene pellet as reference, were recorded on a Perkin-Elmer 580 spectrophotometer equipped with a PE-Infrared Data Station. 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.

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).

The conductivity of 10^{-3} mol dm^{-3} solutions in nitromethane ($\kappa = 5.4 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$) was measured at 20 °C on a Seybold type LTB conductometer.

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

Crystal Data.—$C_{14}H_{23}N_7NiO_6$, $M = 444.15$, monoclinic space group $P2_1/c$, $a = 8.511(3)$, $b = 14.103(3)$, $c = 15.865(8)$ Å, $\beta = 92.75(3)°$, $U = 1\,902.1$ Å^3, $Z = 4$, $D_c = 1.55$ g cm^{-3}, $F(000) = 921$, $\mu(\text{Mo-}K_\alpha) = 10.68\ cm^{-1}$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,73$ Å.

Data Collection and Structure Refinement.—A single crystal of approximate dimensions 0.55 × 0.25 × 0.09 mm, 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 ($11 < \theta < 13°$). *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 $0 \leqslant h \leqslant 9$, $0 \leqslant k \leqslant 16$, and $-18 \leqslant l \leqslant 18$. The scanning rate was adjusted to the required precision of $\sigma(I)/I = 0.01$, with a maximum scan time of 120 s per reflection. Peak counts 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 3 202 reflections were measured, of which 2 978 were independent; from these 1 690 were considered as observed [$I \geqslant 2\sigma(I)$]. Because transmission coefficients varied from 0.80 to 0.97, an absorption correction was applied using a Monte Carlo method as described by DE Graaff.[8] Intensities were corrected for Lorentz and polarization effects. The calculations were performed on the Leiden University Amdahl V7B and IBM 370/158 computers using a local set of computer programs. Scattering factors and anomalous dispersion corrections were taken from ref. 9. The structure was solved by the heavy-atom technique and refined by full-matrix least-squares calculations. The refinement was considered to be complete 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 $R = \Sigma(||F_c| - |F_o||)/\Sigma|F_o|)$ had been reduced to 0.041 and the weighted factor $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ to 0.059. Non-hydrogen atomic co-ordinates are listed in Table 1; bond distances and angles are given in Table 2.

Results and Discussion

Analytical data, *X*-ray powder-diffraction types, conductance data, and melting points of the new compounds are given in Table 3. The low molar conductivities of the metal halide and metal nitrate compounds reveal that in these compounds both anions are bonded to the metal ion. The conductance values of the metal perchlorate compounds lie in the range observed for 1 : 2 electrolytes,[10] indicating the presence of ionic perchlorate groups. Many details in the i.r. spectra of the complexes are characteristic for pyrazole derivatives.[1,12] In the far-i.r. region the vibrational frequencies of the ligand in the co-ordination compounds differ significantly from those observed in the spectrum of the free ligand. However, in some cases consistent patterns are observed and assignments can be made (see below). Bands observed in the regions 255—265 and 360—390 cm^{-1} are tentatively assigned to metal–nitrogen stretching vibrations (pyrazole and ethylamine respectively).[11-14] To obtain information about the precise co-ordination modes of the ligand bdmpae and in order to understand the spectroscopic data, a crystal structure determination of [Ni(bdmpae)(NO_3)$_2$] has been carried out.

Structure of [Ni(bdmpae)(NO_3)$_2$].—The nickel ion is surrounded by three nitrogen and three oxygen atoms in a configuration which can be described as distorted octahedral [Figure (ORTEP projection[15])]. The ligand bdmpae utilizes all its N-donor sites for co-ordination, acting as a tridentate ligand. The nickel–nitrogen distances (Table 2) can be regarded as normal for this type of compound. The N(02)–Ni–N(12) and N(02)–Ni–N(22) angles are *ca.* 80°, and deviate significantly from the ideal co-ordination angle of 90°. The angles made by the Ni–N(12) and Ni–N(22) bonds with the N(12)–C(13) and N(22)–C(23) bonds and with the N(12)–N(11) and N(22)–N(21) bonds (*ca.* 143 and *ca.* 111°, respectively) also deviate significantly from ideal co-ordination angles of *ca.* 125°. It

Table 2. Bond distances (Å) and bond angles (°) for [Ni(bdmpae)$(NO_3)_2$]

Ni–N(02)	2.128(5)	Ni–O(31)	2.052(5)	N(12)–C(13)	1.332(8)	N(22)–C(23)	1.303(8)
Ni–N(12)	2.061(5)	Ni–O(41)	2.157(5)	C(13)–C(14)	1.371(9)	C(23)–C(24)	1.399(10)
Ni–N(22)	2.034(5)	Ni–O(42)	2.145(5)	C(13)–C(16)	1.502(10)	C(23)–C(26)	1.504(10)
N(02)–C(03)	1.515(8)	N(02)–C(10)	1.439(8)	C(14)–C(15)	1.346(9)	C(24)–C(25)	1.342(10)
C(03)–C(04)	1.468(11)	N(02)–C(20)	1.473(8)	C(15)–C(17)	1.498(10)	C(25)–C(27)	1.499(10)
C(10)–N(11)	1.463(8)	C(20)–N(21)	1.466(8)	N(30)–O(31)	1.271(6)	N(40)–O(41)	1.262(7)
N(11)–N(12)	1.351(6)	N(21)–N(22)	1.376(6)	N(30)–O(32)	1.195(7)	N(40)–O(42)	1.263(7)
N(11)–C(15)	1.336(8)	N(21)–C(25)	1.332(8)	N(30)–O(33)	1.264(7)	N(40)–O(43)	1.188(7)

N(02)–Ni–N(12)	80.0(2)	N(12)–Ni–N(22)	161.3(2)	C(10)–N(11)–N(12)	117.3(5)	C(20)–N(21)–N(22)	118.5(5)
N(02)–Ni–N(22)	81.4(2)	N(12)–Ni–O(31)	88.8(2)	C(10)–N(11)–C(15)	130.9(5)	C(20)–N(21)–C(25)	130.6(5)
N(02)–Ni–O(31)	89.6(2)	N(12)–Ni–O(41)	91.4(2)	N(11)–N(12)–C(13)	105.0(5)	N(21)–N(22)–C(23)	105.5(5)
N(02)–Ni–O(41)	100.3(2)	N(12)–Ni–O(42)	97.9(2)	N(12)–C(13)–C(14)	109.7(6)	N(22)–C(23)–C(24)	110.2(6)
N(02)–Ni–O(42)	159.1(2)	O(31)–Ni–O(41)	170.0(2)	C(13)–C(14)–C(15)	107.5(6)	C(23)–C(24)–C(25)	106.3(7)
N(22)–Ni–O(31)	89.4(2)	O(31)–Ni–O(42)	111.2(2)	C(14)–C(15)–N(11)	106.0(6)	C(24)–C(25)–N(21)	107.4(6)
N(22)–Ni–O(41)	93.6(2)	O(41)–Ni–O(42)	58.9(2)	C(16)–C(13)–N(12)	121.4(6)	C(26)–C(23)–N(22)	119.9(6)
N(22)–Ni–O(42)	100.1(2)	Ni–N(02)–C(03)	113.0(4)	C(16)–C(13)–C(14)	128.9(6)	C(26)–C(23)–C(24)	129.8(7)
Ni–N(02)–C(10)	103.5(4)	Ni–N(02)–C(20)	106.0(3)	C(17)–C(15)–N(11)	122.4(6)	C(27)–C(25)–N(21)	121.9(6)
C(03)–N(02)–C(10)	109.1(5)	C(03)–N(02)–C(20)	113.4(5)	C(17)–C(15)–C(14)	131.5(6)	C(27)–C(25)–C(24)	130.7(7)
C(10)–N(02)–C(20)	111.4(5)	N(02)–C(03)–C(04)	115.4(6)	Ni–O(31)–N(30)	116.3(4)	Ni–O(41)–N(40)	93.5(4)
Ni–N(12)–N(11)	110.4(4)	Ni–N(22)–N(21)	111.7(3)	O(31)–N(30)–O(32)	120.1(6)	Ni–O(42)–N(40)	94.0(4)
Ni–N(12)–C(13)	143.2(4)	Ni–N(22)–C(23)	142.6(4)	O(31)–N(30)–O(33)	116.9(6)	O(41)–N(40)–O(42)	113.6(6)
N(02)–C(10)–N(11)	107.6(5)	N(02)–C(20)–N(21)	108.7(5)	O(32)–N(30)–O(33)	123.0(6)	O(41)–N(40)–O(43)	123.0(7)
						O(42)–N(40)–O(43)	123.4(7)

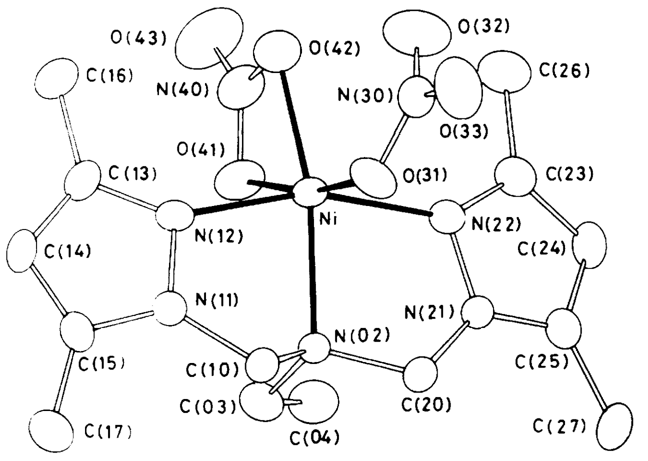

Figure. ORTEP projection and atomic numbering of [Ni(bdmpae)$(NO_3)_2$], hydrogen atoms are omitted

appears that the geometry of the ligand is not very well suited for regular octahedral co-ordination of the nickel ion. It is remarkable that the adaptation to the demands of co-ordination is effected through an adjustment of the co-ordination angles and not through an adjustment of the co-ordination bond lengths. On the other hand, the bond angles around the N(02) atom do not diverge greatly from the ideal tetrahedral angles, probably as a consequence of the symmetrical position of the amine nitrogen in the ligand.

Both pyrazole rings are planar, and the methyl carbon atoms are coplanar with the respective pyrazole rings (distances to the least-squares planes are <0.05 Å). The nickel ion lies in the plane of each pyrazole ring. The two pyrazole rings themselves are not coplanar, the angle between their planes being 17.6(2)°.

Both anions take part in the co-ordination of the nickel ion, one as a monodentate ligand, the other as a bidentate ligand. The i.r. spectrum of this compound also points to these co-ordination modes (see below).

The nickel–oxygen bond lengths lie in the normal range for this type of co-ordination. Both nitrate ions are planar. The very small O(41)–Ni–O(42) bond angle (59°) is clearly imposed by the bidentate co-ordination of this nitrate ion. Again adaptation takes place through adjustment of the bond angles and very little through adjustment of the bond lengths. The nickel ion lies in a plane with N(02), N(12), and N(22) (distances to the least-squares plane are <0.05 Å). The nickel ion lies also in a plane with N(02), O(31), O(41), and O(42) (distances to the least-squares plane are <0.05 Å). These two planes are mutually perpendicular [90.4(1)°], resulting in a so-called *mer* geometry for the NiN_3O_3 octahedron. The packing of the co-ordination units in the crystal lattice is *via* normal van der Waals contacts.

Nitrate Complexes.—The spectral properties of the compound [Ni(bdmpae)$(NO_3)_2$] are consistent with the *X*-ray structure described above. The occurrence of three clearly distinct bands in the i.r. spectrum between 1 700 and 1 800 cm^{-1}, separated by 47 and 20 cm^{-1} (see Table 4), assignable to the $(\nu_1 + \nu_4)$ combination band of the nitrate group, is consistent with the presence of one bidentate and one monodentate nitrate group.[16] A value of 1 075 cm^{-1} obtained for the ligand-field parameter *Dq* (using regular octahedral symmetry for the calculation) is consistent with a N_3O_3 chromophore.[17] *X*-Ray powder-diffraction data show that the bdmpae complexes of nickel, copper, and zinc nitrate are isomorphous (see Table 3). The presence of one bidentate and one monodentate bonded nitrate group in the copper and zinc compounds also follows from the i.r. spectra of these compounds, either through the presence of three $(\nu_1 + \nu_4)$ combination bands,[16] or through the splitting of the normally degenerate ν_3 stretching vibration [18,19] (see Table 4).

E.s.r. measurements on the copper nitrate compound show an exchange-narrowed spectrum (*g* values in Table 5), from which no further structural information could be obtained.[20] The compound [Co(bdmpae)$(NO_3)_2$] exhibits a somewhat complicated ligand-field spectrum, typical neither for six- nor four-co-ordination. It can be best interpreted in terms of a highly distorted six-co-ordinate geometry with an unusually large splitting (*ca.* 3 200 cm^{-1}) of the first transition band (Table 5). From the i.r. spectrum it is clear (Table 4) that also

Table 3. Analytical data, *X*-ray powder-diffraction type, conductance data, and melting points of the complexes with bdmpae

Compound	Colour	Analysis [a] (%) C	H	N	Conductance [b]	Melting point (°C)	*X*-Ray type
[Ni(bdmpae)Cl$_2$]	Green	42.50(43.00)	6.00(5.95)	17.60(17.90)	11.7	215—217	B
[Ni(bdmpae)Br$_2$]	Green	34.95(35.00)	4.95(4.85)	15.00(14.60)	11.6	188—190	B
[Ni(bdmpae)(NO$_3$)$_2$]	Turquoise	38.05(37.85)	5.35(5.25)	21.70(22.10)	25.4	227—228	A
[Ni(bdmpae)$_2$][ClO$_4$]$_2$	Blue	43.05(43.10)	5.95(5.95)	18.15(17.95)	170	209 [c]	—
[Co(bdmpae)Cl$_2$]	Blue	42.65(43.00)	5.90(5.95)	18.30(17.90)	8.7	183—185	C
[Co(bdmpae)Br$_2$]	Blue-purple	35.00(35.00)	4.60(4.85)	14.25(14.30)	6.0	175—177	C
[Co(bdmpae)(NO$_3$)$_2$]	Pink	37.80(37.85)	5.30(5.25)	23.45(22.05)	10.5	201—202	—
[Co(bdmpae)$_2$][ClO$_4$]$_2$	Red-brown	42.85(43.10)	6.00(5.95)	18.20(17.95)	153	164 [c]	—
[Cu(bdmpae)Cl$_2$]·H$_2$O [d] (isomer I)	Green	40.75(41.00)	6.15(6.05)	17.70(16.90)	3.8	178 [c]	—
[Cu(bdmpae)Cl$_2$]·H$_2$O [e] (isomer II)	Green	41.10(40.60)	6.20(6.05)	17.95(16.90)	2.9	178 [c]	—
[Cu(bdmpae)Br$_2$]·H$_2$O [e]	Green	34.35(34.70)	4.70(4.80)	14.80(14.45)	5.3	189—190	—
[Cu(bdmpae)(NO$_3$)$_2$]	Blue	37.50(37.45)	5.30(5.15)	22.25(21.85)	38.7	209—211	A
[Zn(bdmpae)Cl$_2$]	White	42.25(42.30)	5.85(5.85)	18.00(17.60)	5.3	159 [c]	D
[Zn(bdmpae)Br$_2$]	White	34.60(34.55)	4.85(4.75)	14.10(14.40)	5.2	155 [c]	D
[Zn(bdmpae)(NO$_3$)$_2$]	White	37.75(37.70)	5.30(5.15)	22.30(21.75)	3.6	196 [c]	A

[a] Calculated values are in parentheses. [b] Values are in Ω^{-1} cm^2 mol^{-1}. [c] Decomposition temperature. [d] Synthesized following the procedure for [M(bdmpae)X$_2$]; the mono-adduct was isolated. [e] Synthesized following the procedure for [M(bdmpae)$_2$][ClO$_4$]$_2$; the mono-adduct was isolated.

Table 4. Infrared spectral data of the metal–nitrate–bdmpae compounds

	$(\nu_1 + \nu_4)$/cm^{-1}	Δ/cm^{-1}	ν_3/cm^{-1}		Ref.
[Co(bdmpae)(NO$_3$)$_2$]	1 718, 1 730, 1 763	12, 45	1 289, 1 390 (sh) *	Monodentate	16
			1 280 (sh), 1 480	Bidentate	
[Ni(bdmpae)(NO$_3$)$_2$]	1 717, 1 744, 1 764	20, 47	1 312, 1 440	Monodentate	16
			1 290, 1 480	Bidentate	
[Cu(bdmpae)(NO$_3$)$_2$]	1 720, 1 745, 1 755	10, 35	—		16
[Zn(bdmpae)(NO$_3$)$_2$]	1 733, 1 764	31	1 285, 1 478	Bidentate	18
			1 305 (sh), 1 445	Monodentate	

* Observed as a shoulder on a ligand vibration.

Table 5. Ligand-field absorption bands [a] (cm^{-1}) and *X*-band e.s.r. spectral data

[Ni(bdmpae)Cl$_2$]	7 100 (sh), 7 700 (sh), 8 500, 12 300 (sh), 13 700, 19 800, 23 000			
[Ni(bdmpae)Br$_2$]	7 000 (sh), 7 200, 11 700 (sh), 13 400, 19 200 (sh), 22 500			
[Ni(bdmpae)(NO$_3$)$_2$]	7 700 (sh), 10 800, 16 300, 26 300			
[Ni(bdmpae)$_2$][ClO$_4$]$_2$	7 500 (sh), 10 500, 14 800 (sh), 17 500, 27 000			
[Co(bdmpae)Cl$_2$]	5 800 (sh), 10 700, 16 300, 17 800			
[Co(bdmpae)Br$_2$]	5 700 (sh), 10 600, 16 400, 17 400, 25 600			
[Co(bdmpae)(NO$_3$)$_2$]	7 700, 10 900, 14 100, 18 700 (sh), 19 200			
[Co(bdmpae)$_2$][ClO$_4$]$_2$	9 800, 17 400, 19 800 (sh), 21 000			
[Cu(bdmpae)Cl$_2$]·H$_2$O [b]	9 500 (sh), 11 800, 26 700	$g_{\parallel} = 2.27$	$g_{\perp} = 2.07$	
[Cu(bdmpae)Cl$_2$]·H$_2$O [c]	9 800—11 800,[d] 26 900	$g_1 = 2.26$	$g_2 = 2.17$	$g_3 = 2.00$
[Cu(bdmpae)Br$_2$]·H$_2$O [c]	9 700 (t), 11 200	$g_{\parallel} = 2.27$	$g_{\perp} = 2.07$	
[Cu(bdmpae)(NO$_3$)$_2$]	11 100 (sh), 13 500, 28 600	$g_{\parallel} = 2.24$	$g_{\perp} = 2.07$	

[a] (sh) = shoulder, (t) = broad tail. [b] See footnote *d* of Table 3. [c] See footnote *e* of Table 3. [d] Broad maximum from 9 800 to 11 800 cm^{-1}

in this compound one monodentate and one bidentate bonded nitrate group is present.[16] An *X*-ray study [21] of the dichlorocobalt complex of a related ligand, *viz.* bis(3,5-dimethylpyrazol-1-ylmethyl)aniline, reveals that the aniline nitrogen is not bonded to the cobalt ion. In a similar way the ligand bdmpae could also act as a bidentate ligand. Therefore, a structure between square bipyramidal (the oxygen of the bidentate co-ordinating nitrate group in the apical position) and highly distorted octahedral is a reasonable possibility.

Cobalt, Nickel, and Zinc Halide Complexes.—The cobalt, nickel, and zinc chloride and bromide compounds all contain five-co-ordinate metal ions. The evidence for five co-ordination comes from their stoicheiometry, electrical conductance in solution (Table 3), and their electronic spectral properties [22] (Table 5). The chloride and bromide compounds of the same metal ions are isomorphous as powders (see Table 3). This is not the case for chloride and bromide complexes of different metal ions. The ligand-field spectra of the cobalt compounds are typical for high-spin five-co-ordinate cobalt(II) in a distorted trigonal-bipyramidal environment.[23] The far-i.r. spectrum of the cobalt chloride compound shows bands at 302 and 270 cm^{-1} which are in agreement with asymmetric and symmetric Co–Cl stretching vibrations in five-co-ordinate cobalt(II) chloride compounds.[24] In the cobalt bromide compound there appears one band at *ca.* 263 cm^{-1} assignable to the asymmetric Co–Br stretch. The symmetric Co–Br stretch could not be located as it probably occurs below 200 cm^{-1}. The band positions in the diffuse reflectance spectrum of the nickel chloride compound and the shape of the bands occurring at *ca.* 13 700 and *ca.* 23 000 cm^{-1} are in accordance with monomeric high-spin five-co-ordinated nickel(II).[25] The band at *ca.* 250 cm^{-1} in the far-i.r. spectrum of the nickel chloride compound can be assigned to the Ni–Cl stretch. The Ni–Br stretch could not be located as it probably occurs below 200 cm^{-1}. These values lie in the range observed for other five-co-ordinated nickel halide compounds.[13] In the case of the zinc halides, broad bands are observed at 275 and 213 cm^{-1} for the chloride and bromide compound respectively. These values are in good agreement with Zn–X vibrations (X = halide), also suggesting a five-co-ordinated structure.[13,24]

Copper Halide Compounds.—In the case of the [Cu(bdmpae)Cl_2]·H_2O compounds, two different products having the same stoicheiometry could be isolated (see footnotes *d* and *e* of Table 3). Since both chloride ions are co-ordinated to the metal ion (Table 3), a five-co-ordinated structure is possible. E.s.r. measurements on isomer II reveal three *g* values (Table 5) which can be interpreted in terms of a trigonal-bipyramidal structure with a compressed rhombic distortion, having a d_{z^2} ground state.[20] The e.s.r. spectrum of isomer I indicates that in this compound two molecular species are present with their molecular axes mutually perpendicular. This results in an exchange-coupled spectrum with $g_{\parallel} = 2.27$ and $g_{\perp} = 2.07$. Since the latter value is larger than 2.04, the geometry around the copper ion is considered as tetragonally distorted.[20] The diffuse reflectance spectra of both compounds show a main band at *ca.* 11 800 cm^{-1} having a tail on the low-energy side, which is unusual for five-co-ordinate copper(II) compounds, although a distinct shoulder is not always observed.[26] Since the position of this band is too low for six-co-ordinate copper(II) complexes with similar ligands,[22] a five-co-ordinate structure is expected. The ligand-field spectrum of [Cu(bdmpae)Br_2]·H_2O shows a main band at *ca.* 11 200 cm^{-1}, comparable with that of the copper chloride compound. The e.s.r. spectrum of the copper bromide compound reveals exchange coupling and tetragonal distortion of the geometry around the copper ion[20] ($g_{\parallel} = 2.27$ and $g_{\perp} = 2.07$). Since the elemental analyses and electral conductance data (Table 3) are consistent with the formula [Cu(bdmpae)Br_2]·H_2O, a five-co-ordinate geometry is expected conforming to the CuN_3Br_2 chromophore. The presence of water in these copper halides is established from i.r. measurements. All spectra show two bands occurring at *ca.* 3 500 cm^{-1} and *ca.* 3 430 cm^{-1}, due respectively to the asymmetric and the symmetric O–H stretching vibration.[13] Since there is no special evidence for the copper ion to be surrounded by six donor atoms, the water molecules are believed to be present as crystal lattice water. The sharpness of the O–H stretching bands must originate from hydrogen bonding with the halide ions.[27]

Cobalt and Nickel Perchlorate Compounds.—In this case only the compounds having a metal : ligand stoicheiometry of 1 : 2 were isolated. In this respect it must be pointed out that attempts to isolate 1 : 2 compounds of the metal halides and nitrates failed, probably due to steric requirements of the ligand and a greater co-ordinating tendency of the anions. The elemental analyses and conductance data (Table 3) are consistent with their formulation as [M(bdmpae)$_2$][ClO_4]$_2$ (M = Co^{II} or Ni^{II}). With zinc, a hydrolysed product was obtained which will be discussed elsewhere. The compound [Ni(bdmpae)$_2$][ClO_4]$_2$ is a light blue solid, exhibiting ligand-field transitions at 10 500 ($^3T_{2g} \leftarrow {}^3A_{2g}$), 17 500 [$^3T_{1g}(F) \leftarrow {}^3A_{2g}$], 27 000 [$^3T_{1g}(P) \leftarrow {}^3A_{2g}$], and 14 800 cm^{-1} ($^1E_g \leftarrow {}^3A_{2g}$). The positions and shapes of these bands are in good agreement with those reported in the literature for octahedral NiN_6 chromophores.[17,28] The ligand-field spectral parameters calculated[17,22] from these bands are: $Dq = 1\,050$ cm^{-1}, $B = 860$ cm^{-1}, $\beta = 0.83$, and $Dq/B = 1.22$.

The compound [Co(bdmpae)$_2$][ClO_4]$_2$, a red-brown solid, exhibits ligand-field transitions at 9 800 [$^4T_{2g} \leftarrow {}^4T_{1g}(F)$], 19 800 (sh) [$^4A_{2g} \leftarrow {}^4T_{1g}(F)$], and 21 000 cm^{-1} [$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$], in good agreement with an octahedral CoN_6 chromophore.[22,29] The ligand-field spectral parameters calculated[29] from these bands are: $Dq = 1\,065$ cm^{-1}, $B = 830$ cm^{-1}, $\beta = 0.86$, and $Dq/B = 1.28$. Since the second transition band was located only as a shoulder, a recalculation[29] of this band gave a value of 20 100 cm^{-1} which is in good agreement with the assigned value. The band at *ca.* 17 400 cm^{-1} (see Table 5) might be due to the presence of a tetrahedral impurity.*

Conclusions

The present study has shown that interesting new co-ordination compounds may be obtained with the new ligand *NN*-bis(3,5-dimethylpyrazol-1-ylmethyl)aminoethane. This pyrazole derivative acts preferentially as a tridentate ligand through the two nitrogens of each pyrazole ring and the amine nitrogen. Co-ordination of this ligand with metal halides and nitrates results in five-co-ordinate (halides) and six-co-ordinate (nitrates) compounds in which the anions also take part in the co-ordination. With metal perchlorates, six-co-ordinate compounds are obtained (two ligands per metal ion) in which the anions are not bonded to the metal ions.

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* The intensity of the $^4T_1(P) \leftarrow {}^4A_2$ transition band in tetrahedral cobalt(II) species is 15—25 times that of the $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ transition in octahedral cobalt(II) compounds.[22] This provides a rough estimate of the amount of a tetrahedral species present as *ca.* 2%.

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