A Pyrazole Derivative of Aminoethane as a Tridentate Chelating Ligand towards Transition Metals. The *X*-Ray Structure of [*N*,*N*-Bis(pyrazol-1-ylmethyl)aminoethane]dibromocopper(II)†

Jakobert B. J. Veldhuis, Willem L. Driessen,* and Jan Reedijk
Department of Chemistry, Gorlaeus Laboratories, State University Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands

The syntheses and characterization of transition-metal co-ordination compounds containing the newly synthesized ligand *N*,*N*-bis(pyrazol-1-ylmethyl)aminoethane (bpae) are described. The compounds have the general formula [M(bpae)X_2] (M = Co, Cu, Zn, or Cd; X = Cl, Br, or NO_3; M = Ni, X = NO_3) and [M(bpae)$_2$]X_2 (M = Mn, Fe, Co, Ni, Cu, Zn, or Cd; X = BF_4; M = Ni or Cu, X = NO_3). The compounds have been characterized through their spectra and solution conductance. The co-ordination geometries have been deduced to be five-co-ordinate and octahedral. The crystal structure of the green compound [Cu(bpae)Br_2] has been determined by *X*-ray analysis. A monoclinic unit cell with space group $P2_1/c$, a = 9.500(5), b = 11.142(4), c = 13.897(8) Å, β = 93.58(8)°, and Z = 4 was found. The copper atom has a N_3Br_2 chromophore in a distorted square-pyramidal geometry. The apical bromide has a distance of 2.6721(5) Å to the copper ion, the equatorial bromide 2.3841(5) Å. Copper–nitrogen distances are 1.940(2) and 1.957(2) Å for the pyrazole nitrogen-donor atoms and 2.191(2) Å for the amine nitrogen. This geometry is in accord with the spectroscopic results.

Most known ion-exchange polymers do not show a difference in co-ordinating behaviour towards 'harmless' ions, notably Mg^{II} and Ca^{II}, or 'heavy' transition-metal ions.[1,2] Polymers containing heterocyclic N-donor ligands are expected to have a better discriminating ability. The co-ordinating properties of the active sites in chelating ion exchangers are not expected to differ greatly from the co-ordinating properties of the corresponding monomeric systems. Neither pyrazole-containing polymers nor their homogeneous analogues have been investigated systematically,[3] with the exception of the poly(pyrazolyl)borates.[4] A recently reported method for N-substituted pyrazole chelates[5] makes it possible to synthesize a large variety of pyrazole derivatives, *e.g.* *N*,*N*-bis(3,5-dimethylpyrazol-1-ylmethyl)aminoethane,[6] *N*,*N*-bis(3,5-dimethylpyrazol-1-ylmethyl)aminobenzene,[7] and *N*,*N*,*N*-tris(3,5-dimethylpyrazol-1-ylmethyl)amine.[8]

The expectation that a less sterically hindered system would show better discriminating properties and higher capacities led to the present investigation of the potentially tridentate ligand *N*,*N*-bis(pyrazol-1-ylmethyl)aminoethane (bpae). In this paper we report the results obtained with a variety of bivalent transition-metal salts and the ligand bpae. The crystal structure of [Cu(bpae)Br_2] is included to confirm the tridentate chelating nature of the ligand.

Experimental

N,*N*-Bis(pyrazol-1-ylmethyl)aminoethane was synthesized by modification of the procedure described earlier.[5] Solid *N*-hydroxymethylpyrazole (0.5 mol) was mixed with rapid stirring with acetonitrile (50 cm^3) in which it partly dissolved. To this slurry a solution of aminoethane (0.25 mol) in acetonitrile (10 cm^3) was added. A clear solution resulted which was stirred for 48 h. The solvent was removed on a vacuum rotatory evaporator, yielding a slightly yellowish liquid, which was characterized by i.r. and ^{1}H n.m.r. spectroscopy. N.m.r. spectrum [solvent $(CD_3)_2SO$, reference $SiMe_4$, relative intensities in parentheses]: 0.99 (t, 3) and 2.6 (q, 2) (Et), 5.13 (s, 4, bridging Me), 6.29 (t, 2, middle pyrazole H), 7.52 (d, 2) and 7.78 (d, 2) (other pyrazole H).

All hydrated metal salts were of sufficient purity to be used without further purification. All 1:1 (M:L) complexes were synthesized by adding a solution of the ligand (0.05 mol) in absolute ethanol (20 cm^3) to a solution of the metal salt (0.05 mol) in absolute ethanol (20 cm^3) to which triethyl orthoformate (4 cm^3) was added as a dehydrating agent. All 1:2 complexes were synthesized by adding a solution of the metal salt (0.025 mol) in absolute ethanol (20 cm^3) and triethyl orthoformate (4 cm^3) to a solution of the ligand (0.05 mol) in absolute ethanol (20 cm^3). All compounds crystallized upon standing at room temperature. The crystals were collected by filtration, washed with a small amount of absolute ethanol and diethyl ether, and dried *in vacuo* at room temperature. Dark green crystals of [Cu(bpae)Br_2], suitable for *X*-ray analysis, were obtained by recrystallization of the powdered compound from methanol.

Infrared spectra were recorded on a Perkin-Elmer 580 spectrophotometer for Nujol mulls between NaCl discs (4 000—600 cm^{-1}) and polyethylene discs (600—180 cm^{-1}) as well as KBr pellets (4 000—200 cm^{-1}). Solid-state electronic spectra (28 000—5 000 cm^{-1}) were recorded on a Perkin-Elmer 330 spectrophotometer fitted with a reflectance attachment. Electron spin resonance spectra were recorded on a Varian E-3 spectrophotometer for the powdered compounds, at *X*-band frequencies at room temperature and at 77 K (liquid nitrogen).

Metal analyses were carried out complexometrically using ethylenediaminetetra-acetate (edta) as the complexing agent; C, H, and N analyses were performed by University College, Dublin. The conductivity of solutions in nitromethane (10^{-3} mol dm^{-3}) was measured at 25 °C on a Seybold type LTB conductometer.

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† *Supplementary data available* (No. SUP 56390, 5 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.

Non-S. I. unit employed: G = 10^{-4} T.

Crystallography.—*Crystal data.* $C_{10}H_{15}Br_2CuN_5$, M = 428.62, monoclinic, space group $P2_1/c$, a = 9.500(5), b = 11.142(4), c = 13.897(8) Å, β = 93.58(8)°, U = 1 468.4 Å^3, Z = 4, D_c = 1.93 g cm^{-3}, $F(000)$ = 834, $\mu(\text{Mo-}K_\alpha)$ = 7.81 cm^{-1}, $\lambda(\text{Mo-}K_\alpha)$ = 0.710 73 Å.

Data collection and structure refinement. A single crystal of approximate dimensions 0.34 × 0.16 × 0.12 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 ($10 < \theta < 12°$). *X*-Ray intensities were collected on a four-circle Enraf-Nonius diffractometer at room temperature by the ω—θ scan technique for $2 < \theta < 27.5°$ with $-12 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 14$, 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 90 s per reflection. Peak counts were corrected for the background. The instrument and crystal stability were checked every 5 400 s of radiation time by measuring three reference reflections: the observed changes (9%) due to crystal damage were corrected for by a fifth-grade polynomial function. In total 6 719 reflections were measured, of which 3 362 were independent; 2 158 were considered as observed [$I \geqslant 2\sigma(I)$]. An absorption correction was applied using a Monte Carlo method as described by de Graaff.[9] 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. The refinement was considered to be complete when the changes in the parameters were smaller than one third of the standard deviations. The positional and anisotropic thermal parameters of the non-hydrogen atoms were refined. Nine hydrogen atoms were located from Fourier difference maps. The other six hydrogen atoms were positioned at a distance of 0.95 Å from their parent atoms. During the refinement the positions of the hydrogen atoms were coupled to those of their parent atoms. The isotropic thermal parameter for all the hydrogen atoms was kept at the same value, with a final value of 4.8 Å^2.

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 0.024 and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ to 0.025. Non-hydrogen atomic co-ordinates are listed in Table 1, selected bond distances and angles in Table 2.

Table 1. Fractional co-ordinates [× 10^5 for Cu, Br(1), and Br(2), × 10^4 for others] with estimated standard deviations in parentheses for [Cu(bpae)Br$_2$]

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	27 733(4)	17 174(3)	69 055(3)
Br(1)	2 250(3)	21 616(3)	60 567(2)
Br(2)	46 428(3)	23 394(3)	59 523(2)
N(10)	2 013(2)	963(2)	8 233(1)
C(11)	3 203(3)	622(3)	8 930(2)
C(12)	2 752(4)	−22(3)	9 824(2)
C(20)	1 139(3)	1 923(2)	8 588(2)
N(21)	1 884(3)	3 055(2)	8 452(2)
N(22)	2 691(3)	3 158(2)	7 683(2)
C(23)	3 143(3)	4 289(3)	7 706(2)
C(24)	2 624(3)	4 903(3)	8 463(2)
C(25)	1 834(3)	4 099(3)	8 926(2)
C(30)	1 206(3)	−71(3)	7 858(2)
N(31)	2 094(2)	−676(2)	7 202(2)
N(32)	2 788(3)	9(2)	6 577(2)
C(33)	3 466(3)	−755(3)	6 045(2)
C(34)	3 211(4)	−1 919(3)	6 320(2)
C(35)	2 342(3)	−1 840(3)	7 062(2)

Table 2. Selected non-hydrogen bond distances (Å) and bond angles (°) for [Cu(bpae)Br$_2$]

Cu–Br(1)	2.6721(5)
Cu–Br(2)	2.3841(5)
Cu–N(10)	2.191(2)
Cu–N(22)	1.940(2)
Cu–N(32)	1.957(2)
Br(1)–Cu–N(22)	91.47(8)
Br(2)–Cu–N(22)	97.27(7)
Br(1)–Cu–N(32)	95.55(8)
Br(2)–Cu–N(32)	97.87(7)
Br(1)–Cu–Br(2)	112.75(2)
Br(1)–Cu–N(10)	96.06(6)
Br(2)–Cu–N(10)	151.14(6)
N(22)–Cu–N(32)	159.3(1)
N(10)–Cu–N(22)	79.71(9)
N(10)–Cu–N(32)	80.24(9)

Results and Discussion

General.—Colours, analytical data, melting points, *X*-ray diffraction types, and conductance data for the new compounds are given in Table 3. Many details in the i.r. spectra of the compounds are characteristic for pyrazole derivatives.[3,11]

X-Ray diffraction of the powdered samples showed that the manganese and cadmium tetrafluoroborate compounds are mutually isomorphous and that the iron, cobalt, nickel, copper, and zinc tetrafluoroborates are also mutually isomorphous. No isomorphism could be established between the other bpae compounds.

The conductance values for the tetrafluoroborate bpae compounds and for [M(bpae)$_2$][NO$_3$]$_2$ (M = Ni or Cu) lie in the range observed for 1:2 electrolytes,[12] indicating the presence of ionic tetrafluoroborate and nitrate groups, respectively. From these data and from the stoicheiometries and colours it seems highly likely that these compounds are six-co-ordinate. The conductances for the metal halide and the 1:1 metal nitrate bpae compounds lie in the range observed for non-electrolytes, indicating that in these compounds both anions are bonded to the metal ion. The co-ordination numbers in these compounds are five or six (see below).

In the far-i.r. region the vibrational frequencies of the free ligand differ significantly from those observed in the spectra of the co-ordination compounds. However, in the series of isomorphous tetrafluoroborates, consistent patterns are observed and assignments can be made. Bands observed in the region 210—235 cm^{-1} are most likely due to metal–nitrogen stretching vibrations.[13,14]

To obtain more information about the precise co-ordination geometry of the ligand and in order to understand the spectroscopic data, a crystal structure determination for the compound [Cu(bpae)Br$_2$] has been carried out.

Structure of [Cu(bpae)Br$_2$].—The copper ion is surrounded by three nitrogen and two bromine atoms, resulting in a distorted square-pyramidal geometry, rather than a distorted trigonal-bipyramidal geometry (Figure). This is also suggested by the stuctural index τ which has been introduced by Addison *et al.*[15] to show the relative amount of trigonality in five-co-ordinate compounds. For [Cu(bpae)Br$_2$] the value of τ is 0.12 (square pyramid, τ = 0.0; trigonal bipyramid, τ = 1.0). So in this compound the trigonality of the geometry is small. The tridentate ligand bpae utilizes all its potential N-donors for co-

Table 3. Analytical data, conductance values, *X*-ray types, and melting points for bpae compounds

Compound	Colour	Metal analysis (%)[a]	Conductance[b]/ Ω^{-1} cm^2 mol^{-1}	*X*-Ray type[c]	Melting point (°C)
$[Mn(bpae)_2][BF_4]_2$	White	8.9 (8.6)		A	120—122
$[Fe(bpae)_2][BF_4]_2$	Brown	7.8 (8.7)	Insoluble	B	160[d]
$[Ni(bpae)(NO_3)_2]$	Turquoise	15.2 (15.1)	25.1	—	185[d]
$[Ni(bpae)_2][NO_3]_2$	Blue	9.7 (9.9)	90.0	—	143[d]
$[Ni(bpae)_2][BF_4]_2$	Blue	9.3 (9.1)	162	B	205[d]
$[Co(bpae)Cl_2]$	Blue	17.4 (17.6)	10.3	—	164—166
$[Co(bpae)Br_2]$	Blue	13.6 (13.9)	10.1	—	177[d]
$[Co(bpae)(NO_3)_2]$	Purple-red	15.2 (15.2)	14.1	—	143—145
$[Co(bpae)_2][BF_4]_2$	Pink	9.0[e] (9.2)	181	B	198[d]
$[Cu(bpae)Cl_2]$	Green	18.5 (18.7)	5.64	—	174[d]
$[Cu(bpae)Br_2]$	Green	14.8[f] (14.8)	10.9	—	175[d]
$[Cu(bpae)(NO_3)_2]$	Blue	15.9 (16.2)	37.7	—	174[d]
$[Cu(bpae)_2][NO_3]_2$	Blue	9.9 (10.6)	85.3	—	170[d]
$[Cu(bpae)_2][BF_4]_2$	Green	9.8 (9.8)	155	B	159—161
$[Zn(bpae)Cl_2]$	White	20.5[g] (19.4)	4.58	—	180—182
$[Zn(bpae)Br_2]$	White	15.5 (15.2)	6.02	—	172—174
$[Zn(bpae)(NO_3)_2]$	White	17.0 (16.6)	8.5	—	178—180
$[Zn(bpae)_2][BF_4]_2$	White	10.2 (10.1)	176	B	166[d]
$[Cd(bpae)Cl_2]$	White	28.7 (28.9)	5.0	—	165—167
$[Cd(bpae)Br_2]$	White	23.2 (23.5)	5.0	—	142—143
$[Cd(bpae)(NO_3)_2]$	White	25.4 (25.4)	4.5	—	183—185
$[Cd(bpae)_2][BF_4]_2$	White	16.4 (16.1)	174	A	169—171

[a] Calculated values in parentheses. [b] 10^{-3} mol dm^{-3} in CH_3NO_2. [c] Based on powder diffractograms see text. [d] Decomposition temperature. [e] Found: C, 37.3; H, 4.7; N, 22.1. Requires C, 37.4; H, 4.7; N, 21.8%. [f] Found: C, 27.8; H, 3.5; N, 16.2. Requires C, 28.0; H, 3.5; N, 16.3%. [g] Found: C, 35.1; H, 4.4; N, 20.2. Requires C, 35.2; H, 4.4; N, 20.5%.

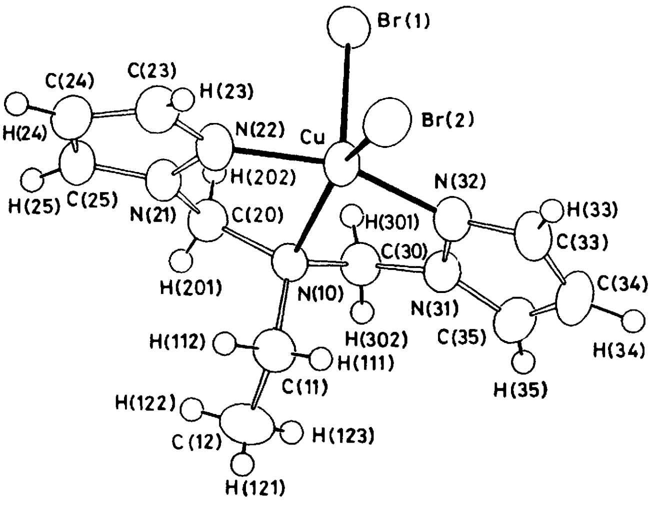

Figure. ORTEP projection of $[Cu(bpae)Br_2]$

ordination. The copper–nitrogen distances are normal for this kind of compound (see Table 2). The apical bromide has a bond distance of 2.6721(5) Å to copper, in the usual range for square-pyramidal geometries.[16] The equatorial bromide, with a distance of 2.3841(5) Å to copper, deforms the ideally square basal plane into a kite-like conformation, and the angles of Br(1)–Cu–Br(2) and N(10)–Cu–Br(2) to respectively 112.75(2) and 151.14(6)°. These angles in fact reflect the distortion towards a trigonal bipyramid. The copper ion lies slightly above the plane formed by the co-ordinating nitrogens (distance to the plane is 0.1 Å) and in the plane formed by Br(1), N(10), Br(2) (0.03 Å).

These planes are mutually perpendicular, the angle between them being 88.5°. Both pyrazole rings are planar. The methyl carbons are coplanar with their parent pyrazole ring (distances to the least-squares planes are less than 0.1 Å). The two pyrazole rings are not mutually coplanar, the angle between the two planes being 18.5°. The pyrazole nitrogen–copper–amine nitrogen angles are about 80°. This behaviour is often observed in ligands which have only two bridging atoms between the co-ordinating atoms, which results in steric constraint. The usual angle of 90° in regular square-pyramidal geometries is thus decreased to 80° by the bite of the ligand, which is too small for this kind of compound.

In the related compound $[Co(Me_5dien)Cl_2]$ (Me_5dien = *N,N,N′,N″,N*″-pentamethyldiethylenetriamine) the geometry[17] is intermediate (τ = 0.45) between square pyramidal (τ = 0.0) and trigonal bipyramidal (τ = 1.0).[15] The observed constraint angle here amounts to about 79°. The ethyl analogue[18] of this compound, $[Co(Et_4dien)Cl_2]$ [Et_4dien = *N,N,N″,N*″-tetraethyldiethylenetriamine), has constraint angles of about 80.5° and a value for τ of 0.77. In spite of this value of τ and the almost equal equatorial bond distances, the authors[18] proposed a distorted square-pyramidal geometry. However, in our opinion a distorted trigonal bipyramid gives a better description of the co-ordination geometry in $[Co(Et_4dien)Cl_2]$.

In the pyrazole derivatives which we have investigated so far the constraint angles are always about 80°, occurring in octahedral[6] and trigonal-bipyramidal[7,8] species. The packing of the co-ordinating units in the crystal lattice proceeds *via* normal van der Waals contacts.

$M(bpae)_2X_2$ *Complexes*.—The tetrafluoroborate and nitrate anions are clearly not bonded to the metal ions in these compounds, as the i.r. frequencies of the anions are characteristic of ionic species.[14,19] The conductance data are in accord with these findings (Table 3). Thus in all compounds $M(bpae)_2X_2$ the metal ions are solely co-ordinated by two chelating bpae ligands.

The shape and position of the ligand-field absorption bands of the cobalt and nickel tetrafluoroborates are characteristic of octahedral geometry (see Table 4). The spectrochemical parameter *Dq* (1 050 and 1 020 cm^{-1} respectively) calculated

Table 4. Ligand-field absorption data (cm^{-1}) for the coloured bpae compounds

[Co(bpae)Cl$_2$]	6 200, 10 500, 16 800, 17 900(sh), 20 400(sh)
[Co(bpae)Br$_2$]	6 100, 10 750, 16 600, 18 100(sh), 19 900(sh)
[Co(bpae)(NO$_3$)$_2$]	8 000, 10 100, 14 900, 19 320, 21 500(sh)
[Co(bpae)$_2$][BF$_4$]$_2$	9 600, 16 900, 19 900, 20 500, 22 000(sh)
[Ni(bpae)(NO$_3$)$_2$]	9 900, 16 030, 25 970
[Ni(bpae)$_2$][NO$_3$]$_2$	10 400, 17 630, 26 380
[Ni(bpae)$_2$][BF$_4$]$_2$	10 200, 17 520, 26 120
[Cu(bpae)Cl$_2$]	9 400(sh), 12 500(br)
[Cu(bpae)Br$_2$]	9 600—13 000(br)
[Cu(bpae)(NO$_3$)$_2$]	10 000(sh), 13 500
[Cu(bpae)$_2$][NO$_3$]$_2$	15 270
[Cu(bpae)$_2$][BF$_4$]$_2$	8 170, 13 350
[(Zn, Co)(bpae)Cl$_2$]	6 100(sh), 7 000, 9 300, 15 100(sh), 15 800, 16 400, 17 400, 20 000(sh)
[(Zn, Co)(bpae)Br$_2$]	6 100(sh), 6 700, 8 600, 15 300, 15 800, 17 100, 19 500(sh)

from these bands (assuming regular octahedral symmetry) is in good agreement with those reported in the literature[20,21] for octahedral CoN$_6$ and NiN$_6$ chromophores. The isomorphous iron, copper, and zinc tetrafluoroborates are thus also six-co-ordinate. It should be realised, however, that this does not imply that, *e.g.*, the metal–amine nitrogen distances are equal to the metal–pyrazole nitrogen donor distances.

The i.r. spectra of the isomorphous cadmium and manganese tetrafluoroborates are quite similar to those of the other tetrafluoroborates. Therefore an octahedral geometry can also be suggested for these compounds, but with a slightly different conformation of the ligand and a different crystal lattice. The slightly larger size of cadmium(II) and manganese(II) probably causes this effect. There must be some distortion of the regular octahedral geometry in all these complexes. The local steric constraints in the ligand, that is the deformation of the octahedral angles between the co-ordinating pyrazole and amine nitrogens to about 80° (see above), account for this distortion.

The e.s.r. spectra of the copper tetrafluoroborate and the copper-doped zinc and cadmium tetrafluoroborates exhibit axial spectra[22] (see Table 5). The axiality, and therefore the axial distortion of the octahedral geometry, can be attributed to a longer bond distance to copper of the weaker amine nitrogen donor than of the pyrazole nitrogen-donor atoms, together with a probable *mer* conformation of the two ligands. Thus an elongation along one axis of the geometry can be proposed as the cause of the axiality of the e.s.r. spectra. A single crystal of the tetrafluoroborate suitable for *X*-ray analysis has been obtained. The crystal structure and the e.s.r. spectra of this compound will be presented later in detail.

The frequencies of the metal–ligand vibrations, which occur in the far-i.r. region of the tetrafluoroborate compounds, the copper compound excepted, lie in a sequence which parallels the Irving–Williams series.[14] The observed metal–nitrogen wavenumbers are: Mn, 215; Fe, 219; Co, 221, Ni, 235; and Zn, 209 cm^{-1}. For the copper tetrafluoroborate a metal–nitrogen frequency could not be assigned.

In the nickel and copper nitrates the metal ions are also in a (slightly distorted) octahedral N$_6$ geometry. This is clear from the i.r. spectra (which for the nickel nitrate is very similar to that of the nickel tetrafluoroborate), the ligand-field spectra (Dq = 1 040 cm^{-1} for the nickel nitrate) and from e.s.r. data for the copper nitrate (see Tables 4 and 5).

The M(bpae)X$_2$ *Compounds.*—The compound [Cu(bpae)Br$_2$] has a distorted square-pyramidal geometry as shown by the crystal structure determination (see above). The low conductivity and the single, broad ligand-field absorption band (see Table 3 and 4 respectively) are consistent with this.[23]

Table 5. *X*-Band e.s.r. data for the powdered copper compounds at room temperature

[Cu(bpae)Cl$_2$]	g_1 = 2.232, g_2 = 2.093, g_3 = 2.052
[Cu(bpae)Br$_2$]	g_1 = 2.188
[Cu(bpae)(NO$_3$)$_2$]	g_1 = 2.257, g_2 = 2.085, g_3 = 2.040
[Cu(bpae)$_2$][NO$_3$]$_2$	$g_{\parallel}$ = 2.258, $g_{\perp}$ = 2.094
[Cu(bpae)$_2$][BF$_4$]$_2$	$g_{\parallel}$ = 2.193, $g_{\perp}$ = 2.047
[Zn(bpae)$_2$][BF$_4$]$_2$^{a,b}	$g_{\parallel}$ = 2.224, $g_{\perp}$ = 2.098, $A_{\parallel}$ = 88 G
[Cd(bpae)$_2$][BF$_4$]$_2$^{b}	$g_{\parallel}$ = 2.268, $g_{\perp}$ = 2.060 $A_{\parallel}$ = 146 G

[a] Spectrum changes upon cooling (see text). [b] 1% Cu-doped.

In the far-i.r. spectrum of the compound no bands due to metal–bromide vibrations were found and probably occur below 180 cm^{-1}. The e.s.r. measurements show one broad band at g = 2.188. Apparently, this is due to exchange coupling of the misaligned CuN$_3$Br$_2$ chromophores in the unit cell. In the unit cell the main axes of two pairs of the distorted square pyramids point roughly in opposite directions; the two main axes within each pair are not quite parallel. On the other hand, the e.s.r. spectrum of the five-co-ordinate copper chloride shows three g values (Table 5) which can be interpreted in terms of a distorted trigonal or distorted square-pyramidal geometry with a $d_{x^2-y^2}$ ground state.[16] The ligand-field spectrum, with a distinct shoulder on the low-energy side of the absorption band, is consistent with this.[24] The Cu–Cl frequency was located as one strong band at 297 cm^{-1}.

With the nickel halides, compounds were obtained containing bpae and decomposition products of bpae. Analyses (C, H, and N) of the chloride compound suggested the composition Ni(bpae)(pyrazole)Cl$_2$. Apparently the strong preference of bivalent nickel for an octahedral co-ordination geometry results in partial decomposition of the ligand bpae through hydrolysis. This kind of decomposition has been observed in similar pyrazole derivatives and confirmed by a crystal structure.[25] These decomposition products will be discussed in detail elsewhere.[26]

The cobalt chloride and bromide compounds are very similar. In both cases the anions are bonded to the metal ions, as is demonstrated by the very low conductance in nitromethane (see Table 3). The M–X vibrations at 305 and 255 cm^{-1} (Co–Cl) and 260 and 233 cm^{-1} (Co–Br) are in good agreement with those found for other five-co-ordinate cobalt halide species.[27] The ligand-field absorption bands (see Table 4) also indicate a five-co-ordinate cobalt ion.[28,29]

The zinc bromide and chloride compounds are not mutually *X*-ray isomorphous but have very similar i.r. spectra. The ligand-field spectra of the 5% cobalt-doped zinc halides also indicate five-co-ordinate species. This is consistent with the non-electrolyte behaviour (see Table 3), both halide ions and all three ligand nitrogen-donor atoms being co-ordinated to the zinc ion. The Zn–X frequencies (Zn–Cl, 317 and 291; Zn–Br, 240 and 210 cm^{-1}) are in agreement with values reported for five-co-ordinate zinc compounds.[28] The ligand-field spectra of the 5% cobalt-doped cadmium chloride and bromide compounds, on the other hand, indicate distinct octahedral species. The conductance data of the compounds reveal non-electrolyte behaviour, and the far-i.r. spectrum of the chloride has a very broad and strong band at 215 cm^{-1}. The cadmium bromide vibration frequencies probably occur below 180 cm^{-1}. These data are consistent with a polymeric species in which terminal halide bands occur.[14] Therefore, we assume a polymeric structure with half of the halide ions bridging between cadmium ions and the other half terminally co-ordinated. The low solubility in nitromethane and the

Table 6. Some i.r. data (cm^{-1}) for the metal nitrates

Compound	($\nu_1 + \nu_4$)	Δ	ν_3	
[Co(bpae)(NO_3)$_2$]	1 761, 1 721	40	1 495, 1 297	See text
[Ni(bpae)(NO_3)$_2$]	1 762, 1 717	45	1 497, 1 278	Bidentate
	1 762, 1 745	17	1 405, 1 304	Unidentate
[Ni(bpae)$_2$][NO_3]$_2$	1 741		1 347	Ionic
[Cu(bpae)(NO_3)$_2$]	1 762, 1 712	50	1 482, 1 270	Bidentate
	1 745, 1 722	23	1 410, 1 310	Unidentate
[Cu(bpae)$_2$][NO_3]$_2$	1 748		1 371	Ionic
[Zn(bpae)(NO_3)$_2$]	1 768, 1 720	48	1 496, 1 292	Bidentate
	1 755, 1 739	16	1 410, 1 319	Unidentate
[Cd(bpae)(NO_3)$_2$]	1 770, 1 713	57	1 465, 1 275	Bidentate
	1 750, 1 730	20	1 445, 1 305	Unidentate

instantaneous crystallization of the cadmium chloride and bromide bpae compounds are in accord with this.

Most of the nitrate compounds have a distorted octahedral co-ordination geometry, as is clear from their electronic spectra, conductance data, and i.r. spectra. For the nickel nitrate there are three distinct $\nu_1 + \nu_4$ combination bands between 1 700 and 1 800 cm^{-1} (see Table 6) separated by 45 and 17 cm^{-1}. This is consistent with one unidentate and one bidentate nitrate group.[30] The value of 990 cm^{-1} obtained for the ligand field parameter *Dq* (assuming regular octahedral symmetry) is in accord with those of nickel compounds having a N_3O_3 chromophore.[6,21] The presence of one bi- and one uni-dentate co-ordinating nitrate group in the copper, zinc, and cadmium compounds also follows from their i.r. through the occurrence of four $\nu_1 + \nu_4$ combination bands (see Table 6).

E.s.r. measurements on the copper nitrate show a rhombic spectrum which can be interpreted in terms of a copper ion in an elongated rhombic octahedral environment (Table 5). The cobalt nitrate, however, has a ligand-field spectrum which is typical of five-co-ordinate cobalt compounds,[29,31] denoting a N_3O_2 chromophore. This is not consistent with the i.r. data (see Table 6), which suggest the presence of two bidentate nitrate ions. The discrepancy could be understood by assuming that the nitrate ions are either unidentate but bound very strongly to the cobalt ion or anisobidentate. The magnetic measurements on this compound rendered a slightly temperature-dependent $\mu_{eff.}$ of 4.29 at room temperature and 4.17 at 90 K. Similar low values for five-co-ordinate cobalt have been reported earlier for high-spin cobalt compounds.[32]

Conclusions

The present study has shown that with the ligand *N,N*-bis(pyrazol-1-ylmethyl)aminoethane a variety of interesting co-ordination compounds can be formed. In these compounds the ligand always uses the pyrazole nitrogen-donor atoms and the tertiary amine nitrogen atom for co-ordination and so behaves solely as a tridentate ligand. Co-ordination of this ligand with metal ions results in the formation of five-co-ordinate (halides) and six-co-ordinate (nitrates) compounds in which the anions also take part in the co-ordination. Six-co-ordinate compounds are obtained with the metal tetrafluoroborates (two ligands per metal ion) in which the anions do not co-ordinate to the metal ion.

The ready formation of the reported compounds and the low affinity of this ligand towards nickel ions suggests that the analogous polymer-anchored group will be a discriminating chelating ion exchanger.

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