Transition metal compounds of the tridentate pyrazole substituted amine ligand bis(2-(3,5-dimethyl-1-pyrazolyl)ethyl)ethylamine (ddae). X-ray structures of $[Co(ddae)(NO_3)_2]$, $[Cu(ddae)(NO_3)(H_2O)](NO_3)$ and $[Cu(ddae)(Cl)_2]\cdot C_2H_5OH$

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Abstract

Six new compounds of the ligand bis(2-(3,5-dimethyl-1-pyrazolyl)ethyl)ethylamine (ddae), viz $[Co(ddae)(NO_3)_2]$, $[Ni(ddae)(NO_3)_2]$, $[Cu(ddae)(Cl)_2]$ (C_2H_5OH), $[Cu(ddae)(NO_3)(H_2O)](NO_3)$, $[Ni(ddae)(H_2O)(BF_4)_2]$ and $[Cu(ddae)(F)(BF_4)]$ are described These transition metal compounds are mononuclear In all cases ddae acts as a tridentate ligand The cobalt and nickel nitrates are isomorphous, otherwise these compounds all have different structures. The compound $[Cu(ddae)Cl_2]\cdot C_2H_5OH$ crystallizes in the monoclinic space group $P2_1/c$ with $a=8.327(1)$, $b=14.782(2)$, $c=18.654(3)$ Å, $\beta=96.53(1)°$ and $Z=4$. The structure was solved by heavy-atom methods and refined by least-squares methods to a residual R of 0.048 ($R_w=0.081$) for 2787 significant reflections. The asymmetric unit comprises the whole formula unit. The surrounding geometry of the Cu(II) ion is distorted square-pyramidal with the two pyrazole nitrogens (Cu–N distances 1.984(4) and 1.999(4) Å) and the two chloride ions (Cu–Cl distances 2.322(2) and 2.400(2) Å) in a square and the amine nitrogen (Cu–N distance 2.181(4) Å) at the apex. The ligand is coordinated in a *mer* geometry. The ethanol molecule is hydrogen bonded to one of the chloride ions with a Cl–O distance of 3.24(1) Å. The compound $[Cu(ddae)(NO_3)(H_2O)](NO_3)$ crystallizes in the orthorhombic space group $Pna2_1$ with $a=24.984(5)$, $b=10.798(2)$, $c=8.466(3)$ Å and $Z=4$. The structure was solved by heavy-atom methods and refined by least-squares methods to a residual R of 0.048 ($R_w=0.069$) for 960 significant reflections. The asymmetric unit comprises the whole formula unit. The Cu(II) ion is in a distorted square-pyramidal environment of the two pyrazole nitrogens at 2.00(1) and 2.01(1) Å, a water oxygen atom at 1.938(9) Å, and an oxygen atom of one of the nitrate ions at 2.00(1) Å in a square, and the amine nitrogen at 2.34(1) Å at the apex. The ligand is folded and coordinated in a *fac* geometry. If the nitrate ion was regarded as bidentate-coordinate with the rather too long Cu–O distance of 2.63(1) Å, then the copper ion would be in a strongly distorted octahedral environment. The water molecule is hydrogen bonded to the non-coordinated nitrate ion in two different, symmetry related, positions, with O–O distances of 2.74(1) and 2.81(2) Å, in such a way that the complex cations are linked together in a chain. The compound $[Co(ddae)(NO_3)_2]$ crystallizes in the monoclinic space group $P2_1/c$ with $a=16.351(3)$, $b=15.708(2)$, $c=8.484(1)$ Å, $\beta=104.78(1)°$ and $Z=4$ The structure was solved by heavy-atom methods and refined by least-squares methods to a residual R of 0.077 ($R_w=0.065$) for 1502 significant reflections. The asymmetric unit comprises the whole formula unit. The surrounding geometry of the Co(II) ion is distorted octahedral, with the ligand folded in a *fac* geometry with the N(amine) at 2.209(9) Å and the N(pyrazoles) at 2.030(10) and 2.112(9) Å. One of the nitrate ions is monodentate with Co–O of 2.060(8), the other nitrate is quite symmetrically bidentate coordinated to the cobalt ion with Co–O distances of 2 172(8) and 2.216(8) Å.

Key words: Crystal structures; Copper complexes; Tridentate ligand complexes; Chelate complexes

Introduction

To gain insight into the coordination behaviour of larger ligand systems containing both pyrazole groups and amine nitrogens as potential N-donor atoms we have developed synthetic routes [1–3] which enable us to obtain ligands which vary in denticity and steric constraints. This research effort is directed to the modelling of metallo-enzymes, such as type III copper proteins [4], and to the incorporation of these ligand systems on polymeric backbones and silica to function as chelating ion exchangers with a high degree of

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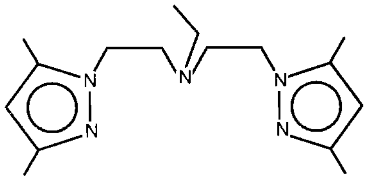

Fig. 1. Bis(2-(3,5-dimethyl-1-pyrazolyl)ethyl)ethylamine (ddae).

selectivity [5]. In the present study some new coordination compounds of the ligand bis(2-(3,5-dimethyl-1-pyrazolyl)ethyl)ethylamine (ddae), see Fig. 1, are described. This ligand is rather bulky, due to the methyl substituents on the pyrazole groups. At the same time, this ligand is quite flexible, due to the ethyl groups which connect the amine N-donor to N1 of the pyrazole groups thereby creating a four-bond ligand bite which enables the ligand to form six-membered chelate rings upon coordination to a metal ion. In earlier reports we described analogous ligands with unsubstituted pyrazole groups and three-bond ligand bites [6, 7]. To establish the coordination mode of ddae and its conformation X-ray crystal structures of three representative ddae compounds are presented.

Experimental

All reagents were commercially available and were of sufficient purity.

The ligand bis(2-(3,5-dimethyl-1-pyrazolyl)ethyl)-ethylamine, abbreviated ddae (see Fig. 1), was synthesized after a method reported by Haanstra *et al.* [2, 3]. 0.01 mol of the hydrochloric salt of ethylamine and 0.21 mol O-tosylated 2-(3,5-dimethyl-1-pyrazolyl)ethanol were mixed with a solution of 13.5 g NaOH in 120 ml of water and refluxed for about 4 h. After cooling, the mixture was extracted three times with 120 ml trichloromethane. The trichloromethane layers were gathered, dried with anhydrous calcium sulfate and

TABLE 1 Crystal and refinement data for the compounds $[Cu(ddae)Cl_2]\cdot C_2H_5OH$ (**A**), $[Cu(ddae)(NO_3)(H_2O)](NO_3)$ (**B**) and $[Co(ddae)(NO_3)_2]$ (**C**)

	A	**B**	**C**
Formula	$C_{18}H_{33}Cl_2CuN_5O$	$C_{16}H_{29}CuN_7O_7$	$C_{16}H_{27}CoN_7O_6$
M	469.94	494.99	472.37
a (Å)	8.327(1)	24.984(5)	16.351(3)
b (Å)	14.782(2)	10.798(2)	15.708(2)
c (Å)	18.654(3)	8.466(3)	8.484(1)
α (°)	90.0	90.0	90.0
β (°)	96.53(1)	90.0	104.78(1)
γ (°)	90.0	90.0	90.0
U (Å^{-3})	2281.2	2283.9	2106.8
F(000)	988	1036	988
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$Pna2_1$	$P2_1/c$
Z	4	4	4
D_c (g cm^{-3})	1.36	1.43	1.48
μ (cm^{-1})	12.0	10.0	70.6
Crystal dimensions	0.4×0.3×0.2	0.5×0.2×0.1	0.5×0.1×0.1
Colour	green	blue	brick red
Habit	needle	needle	needle
Radiation	Mo Kα	Mo Kα	Cu Kα
λ (Å)	0.710730	0.710730	1.54178
h Values	−10 to 10	0 to 29	−18 to 18
k Values	0 to 19	0 to 12	0 to 17
l Values	0 to 24	0 to 10	−9 to 0
Scan range, θ (°)	2–27	2–25	2.5–60
Transmission factors	0.96–1.04	0.89–1.08	0.71–1.32
Intensity variations	4.97	4.98	2.89
No. measured reflections	5595	2335	3275
No. unique reflections	5437	2332	3273
No. used in refinement ($I > 2\sigma(I)$)	2787	960	1502
Total no. parameters	244	130	272
R_f	0.048	0.048	0.077
R_w	0.081	0.069	0.065
Goodness of fit	0.781	0.648	2.67
Max., min $\Delta\rho$ excursions (e Å^{-3})	1.03/−0.54	0.60/−0.32	0.83/−1.00

filtered. The solvent was then removed on a rotary evaporator, rendering a brownish yellow oil, yield 95%. This oil was used without further purification.

^{1}H NMR (ppm), solvent = $CDCl_3$: 0.98, triplet (3H); 2.18, singlet (12H); 2.56, multiplet (2H); 2.82, triplet (4H); 3.84, triplet (4H); 5.74, singlet (2H).

The coordination compounds were prepared by dissolving 2 mmol hydrated metal salt in 4 ml triethylorthoformate and 20 ml ethanol and adding to this solution 1.5 g ddae in 5 ml ethanol. After crystallization, the products were collected by filtration and washed with very little ethanol and some diethyl ether.

The metal content was determined complexometrically using Na_2H_2edta as complexing agent. Chloride contents were determined potentiometrically with $AgNO_3$ as the precipitating agent [8]. C, H and N analyses were performed at University College, Dublin.

IR spectra of the compounds pelleted in KBr were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 580 spectrophotometer, equipped with a PE data station.

Solid-state electronic spectra (30 000–5000 cm^{-1}) were recorded on a Perkin-Elmer 330 spectrophotometer fitted with a diffuse reflectance attachment, using MgO as a reference.

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

X-ray powder photographs were taken on a Guinier-type diffractometer.

Crystallographic data collection and structure refinement

The diffraction data for $[Cu(ddae)Cl_2]\cdot C_2H_5OH$ (**A**), $[Cu(ddae)(NO_3)H_2O](NO_3)$ (**B**) and $[Co(ddae)(NO_3)_2]$ (**C**) were collected at room temperature on a four-circle Enraf-Nonius CAD4 diffractometer. Crystal data and additional details of the data collection and refinement of the structures are summarized in Table 1. The intensities of the reflections were corrected for Lorentz and polarization effects. Empirical absorption correction was applied with the program DIFABS [9]. The calculations were performed on the Leiden University Amdahl 5860 computer using a local set of computer programs. Scattering factors were taken from the International Tables for X-ray Crystallography [10]. The positions of the heavy atoms in the structures were located from a Patterson map. The other non-hydrogen atoms were located with the program AUTOFOUR [11]. The structures were refined by full-matrix least-squares. The hydrogen atoms of **A**, **C** and all but two of **B** were placed at 0.95 Å from their parent atoms. One hydrogen atom of **B**, H51, was found from Fourier difference maps, the other H atom of the water molecule was not found and could not be placed. The non-hydrogen atoms of **A** and **C** were refined anisotropically. For **B** only the copper atom was refined anisotropically, which could not be performed for all non-hydrogen atoms in view of the limited number of significant reflections. In all compounds the positional parameters of the hydrogen atoms were coupled to their parent atoms and the thermal parameters of the H atoms were coupled to one another, as were the thermal parameters of the non-hydrogen atoms of the ethanol molecule of **A**, and refined isotropically. The function minimized was $\Sigma w(\|F_o| - |F_c\|)^2$, where $w = 1/\sigma^2(F)$. The fractional coordinates of the non-hydrogen atoms of **A**, **B** and **C** are listed in Table 2. Selected bond distances, angles and hydrogen bond distances are given in Table 3. See also 'Supplementary material'.

TABLE 2. Fractional coordinates (Cu $\times 10^5$, others $\times 10^4$) and equivalent isotropic thermal parameters (Cu, Cl Å^2 $\times 10^2$, others Å^2 $\times 10$) of the non-hydrogen atoms of $[Cu(ddae)Cl_2]$ C_2H_5OH (**A**), $[Cu(ddae)(NO_3)H_2O](NO_3)$ (**B**) and $[Co(ddae)(NO_3)_2]$ (**C**)

Atom	*x/a*	*y/b*	*z/c*	B_{eq}^{a}
A				
Cu1	91910(12)	35941(7)	35466(5)	297(2)
Cl5	7336(1)	4118(1)	4290(1)	441(4)
Cl6	10070(2)	3433(1)	2372(1)	552(5)
N2	11075(5)	2856(3)	4214(2)	32(1)
C3	10739(6)	2883(4)	4977(3)	43(2)
C4	11923(8)	2393(6)	5512(4)	66(2)
N11	11962(5)	4883(3)	3869(2)	28(1)
N12	10358(5)	4766(3)	3626(2)	30(1)
C13	9892(6)	5531(3)	3288(3)	37(1)
C14	11163(7)	6150(4)	3330(3)	41(1)
C15	12454(6)	5732(3)	3701(3)	33(1)
C16	8211(7)	5648(5)	2920(4)	55(2)
C17	14122(7)	6058(4)	3937(3)	44(2)
C18	12837(6)	4243(3)	4363(3)	36(1)
C19	12656(6)	3264(3)	4119(3)	37(1)
N21	8214(6)	1615(3)	3544(3)	41(1)
N22	7835(5)	2489(3)	3338(3)	39(1)
C23	6356(6)	2455(4)	2996(3)	43(2)
C24	5769(8)	1592(5)	2977(4)	55(2)
C25	6987(8)	1058(5)	3323(4)	52(2)
C26	5590(8)	3283(5)	2652(4)	61(2)
C27	7106(11)	54(5)	3475(6)	85(3)
C28	9716(8)	1342(4)	3982(4)	54(2)
C29	11134(7)	1924(4)	3919(4)	50(2)
O7	8756(14)	820(7)	5780(6)	159(2)
C8	726(2)	63(1)	579(1)	159(2)
C9	6435(22)	1384(10)	5413(10)	159(2)
B				
Cu1	14264(4)	14384(9)	24990(0)	256(3)
N2	1488(4)	−342(10)	4069(14)	31(2)

(continued)

TABLE 2 (*continued*)

Atom	*x/a*	*y/b*	*z/c*	B_{eq}[a]
C3	1286(5)	−1394(12)	3131(18)	36(3)
C4	1222(7)	−2612(17)	3937(28)	65(4)
N11	913(4)	2113(9)	5622(14)	27(2)
N12	978(4)	2425(10)	4038(14)	30(2)
C13	658(5)	3361(12)	3794(18)	29(2)
C14	392(6)	3649(16)	5183(21)	46(3)
C15	571(6)	2884(14)	6325(21)	42(3)
C16	598(6)	3957(13)	2222(19)	41(3)
C17	417(8)	2739(19)	8009(26)	71(5)
C18	1219(6)	1093(13)	6325(21)	39(3)
C19	1156(6)	−136(14)	5514(20)	40(3)
N21	2546(4)	1176(9)	3446(15)	32(2)
N22	2135(4)	2004(10)	3337(14)	26(2)
C23	2364(6)	3123(14)	3682(20)	34(2)
C24	2899(6)	2969(15)	3882(22)	44(3)
C25	3027(5)	1773(12)	3752(19)	30(2)
C26	2016(6)	4232(17)	3665(24)	51(3)
C27	3518(6)	1079(17)	3750(26)	59(4)
C28	2445(6)	−160(12)	3326(19)	38(3)
C29	2050(5)	−565(13)	4537(20)	36(3)
N30	1906(4)	1916(10)	−254(15)	31(2)
O31	1808(4)	943(9)	518(13)	33(1)
O32	1691(4)	2888(9)	140(14)	46(2)
O33	2205(4)	1852(10)	−1393(15)	47(2)
N40	399(5)	−1121(12)	−1502(18)	44(2)
O41	811(4)	−928(10)	−609(15)	51(2)
O42	−51(6)	346(12)	3546(18)	68(3)
O43	397(4)	−2013(11)	−2372(24)	70(2)
O5	763(3)	1039(8)	1429(12)	32(1)
C				
Co1	2508(1)	92(1)	1365(2)	122(5)
N2	2317(6)	−739(6)	−799(11)	17(3)
C3	2304(9)	−1665(8)	−336(14)	35(4)
C4	1589(9)	−1869(8)	440(15)	50(5)
N11	3803(6)	698(6)	−400(11)	20(3)
N12	3604(5)	610(6)	1096(9)	18(3)
C13	4256(8)	1015(8)	2113(13)	23(4)
C14	4810(7)	1389(8)	1346(15)	27(4)
C15	4495(9)	1162(8)	−279(15)	28(4)
C16	4287(7)	1042(8)	3929(12)	42(5)
C17	4836(7)	1396(8)	−1734(13)	45(5)
C18	3262(8)	279(8)	−1832(13)	32(4)
C19	3074(8)	−637(8)	−1452(12)	28(4)
N21	1069(6)	829(7)	−1336(12)	24(3)
N22	1790(6)	1045(6)	−124(11)	16(3)
C23	1840(9)	1913(9)	−131(15)	25(4)
C24	1142(9)	2213(8)	−1355(16)	35(5)
C25	663(9)	1516(10)	−2155(15)	34(5)
C26	2531(8)	2387(7)	953(13)	35(4)
C27	−81(7)	1465(8)	−3568(13)	43(4)
C28	849(7)	−86(8)	−1633(12)	29(4)
C29	1538(7)	−571(8)	−2134(13)	28(4)
N30	1627(7)	439(6)	3465(13)	30(4)
O31	2346(5)	746(5)	3580(8)	26(2)
O32	1377(5)	−73(6)	2230(9)	35(3)
O33	1192(6)	571(6)	4376(11)	23(3)
N40	3131(8)	−1210(8)	4073(16)	43(4)
O41	3251(5)	−821(5)	2789(9)	31(3)
O42	3689(6)	−1735(8)	4639(14)	98(5)
O43	2509(8)	−1139(8)	4522(13)	35(4)

[a] $B_{eq} = 8/3\ \pi^2$ trace U

TABLE 3 Selected bond lengths (Å) and bond angles (°) of the non-hydrogen atoms of [Cu(ddae)Cl$_2$] C$_2$H$_5$OH (**A**), [Cu(ddae)(NO$_3$)H$_2$O](NO$_3$) (**B**) and [Co(ddae)(NO$_3$)$_2$] (**C**)

A			
Cu1–Cl5	2.322(2)	Cl6–Cu1–N22	88.0(1)
Cu1–Cl6	2.400(2)	N2–Cu1–N12	94.6(1)
Cu1–N2	2.181(4)	N2–Cu1–N22	93.2(2)
Cu1–N12	1.984(4)	N12–Cu1–N22	171.6(2)
Cu1–N22	1.999(4)	Cu1–N2–C19	108.7(3)
		Cu1–N2–C29	107.7(3)
Cl5–Cu1–Cl6	150.53(6)	Cu1–N2–C3	109.4(3)
Cl5–Cu1–N2	108.1(1)	Cu1–N12–N11	125.8(3)
Cl5–Cu1–N12	91.0(1)	Cu1–N12–C13	126.4(3)
Cl5–Cu1–N22	89.4(1)	Cu1–N22–N21	127.4(3)
Cl6–Cu1–N2	101.4(1)	Cu1–N22–C23	126.9(4)
Cl6–Cu1–N12	87.5(1)	O7–C8–C9	103(2)
B[a]			
Cu1–N2	2.34(1)	O5–Cu1–O32	89.6(4)
Cu1–N12	2.02(1)	N2–Cu1–N12	95.9(4)
Cu1–N22	2.00(1)	N2–Cu1–N22	89.5(4)
Cu1–O31	2.00(1)	N2–Cu1–O31	103.0(4)
Cu1–O32	2.62(1)	N2–Cu1–O5	98.0(4)
Cu1–O5	1.94(1)	N12–Cu1–N22	95.8(4)
O5–O41′	2.74(2)	N12–Cu1–O31	160.8(4)
O5–O42″	2.74(2)	N12–Cu1–O5	86.8(4)
O31–Cu1–O32	53.2(4)	N22–Cu1–O31	87.5(4)
N12–Cu1–O32	108.4(4)	N22–Cu1–O5	171.8(4)
N22–Cu1–O32	82.2(4)	O31–Cu1–O5	87.5(4)
N2–Cu1–O32	154.9(4)	Cu1–O5–O42″	112(1)
Cu1–O5–O41′	115(1)	O41′–O5–O42″	103(1)
C			
Co1–N12	2.03(1)	N2–Co1–N22	89.0(3)
Co1–N2	2.209(9)	N2–Co1–O32	105.0(3)
Co1–N22	2.112(9)	N2–Co1–O41	90.8(3)
Co1–O31	2.216(8)	N22–Co1–O32	84.0(4)
Co1–O32	2.172(8)	N22–Co1–O41	177.7(4)
Co1–O41	2.060(8)	O32–Co1–O41	98.3(3)
		O31–Co1–N12	102.1(3)
N12–Co1–N2	94.9(4)	O31–Co1–N2	163.1(4)
N12–Co1–N22	91.2(4)	O31–Co1–N22	90.6(3)
N12–Co1–O32	159.5(3)	O31–Co1–O32	58.2(3)
N12–Co1–O41	86.6(3)	O31–Co1–O41	90.3(3)

[a] $' = \frac{1}{2} - x,\ \frac{1}{2} - y,\ \frac{1}{2} - z.\ '' = \frac{1}{2} - x,\ \frac{1}{2} - y,\ z$

Results and discussion

Description of the X-ray structures

The asymmetric unit of [Cu(ddae)Cl$_2$]·C$_2$H$_5$OH equals the formula unit. The environment of the Cu(II) ion, see Fig. 2, is distorted square-pyramidal with the two pyrazole nitrogens, at 1.984(4) and 1.999(4) Å, and the two chloride ions, at 2.322(2) and 2.400(2) Å in the square and the amine nitrogen at 2.181(4) Å at the apex. The ligand is straight and occupies the apex of the square pyramid and two *trans* positions in the square, viz. in a *mer* conformation. The ethanol molecule is hydrogen bonded to one of the chloride ions with a Cl–O distance of 3.24(1) Å. The distortion from

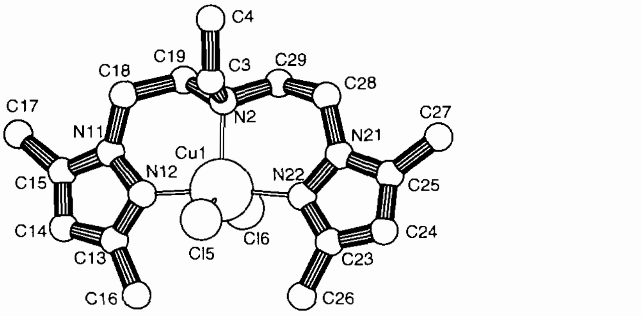

Fig. 2. PLUTON [12] projection of $[Cu(ddae)Cl_2]$ C_2H_5OH (**A**), for clarity the ethanol molecule and the H atoms are omitted

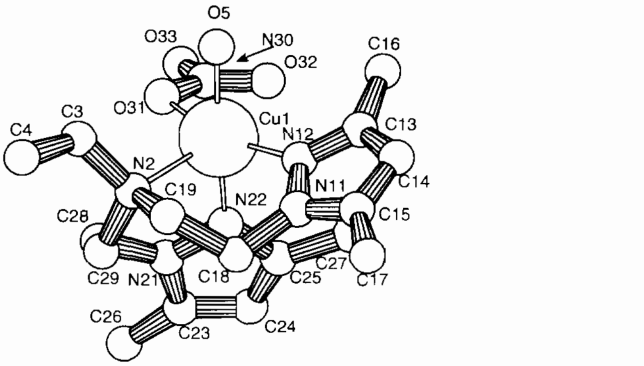

Fig. 3. PLUTON [12] projection of $[Cu(ddae)(NO_3)H_2O](NO_3)$ (**B**), for clarity the non-coordinated nitrate ion and the H atoms are omitted.

square-pyramidal can be described as $\tau = 0.35$, being between the values of $\tau = 0.0$ for a regular square pyramid and $\tau = 1.0$ for a regular trigonal bipyramid, after Addison *et al.* [13].

The formula $[Cu(ddae)(NO_3)(H_2O)](NO_3)$ fits the asymmetric unit. The Cu(II) ion, see Fig. 3, is in a not so much ($\tau = 0.18$) distorted square-pyramidal environment of the two pyrazole nitrogens at 2.00(1) and 2.01(1) Å, a water oxygen atom at 1.938(9) Å, and an oxygen atom of one of the nitrate ions at 2.00(1) Å in a square, and the amine nitrogen at 2.34(1) Å at the apex. The ligand is folded and occupies one face of the square pyramid, viz. in a *fac* conformation. Should the nitrate ion be regarded as bidentate coordinate with the rather too long Cu–O distance of 2.63(1) Å, then the copper ion is in a strongly distorted octahedral environment. The water molecule is hydrogen bonded, through an H atom (H51) which was located in a Fourier map, to O41′ of the non-coordinated nitrate ion with an O–O distance of 2.74(1) Å. The distance of O5 to O42″ is only slightly longer, viz. 2.81(2) Å (see Table 2), suggesting another H bond, which is substantiated by the angles around O5, viz. O41′-O5-O42″ = 103(1), Cu1-O5-O41′ = 115(1), Cu1-O5-O42″ = 112(1)°. These hydrogen bonds link the cations into chains.

The asymmetric unit of $[Co(ddae)(NO_3)_2]$ comprises the whole formula unit, see Fig. 4. The surrounding geometry of the Co(II) ion is distorted octahedral. The ligand is in the *mer* conformation with the N(amine) at 2.209(9) Å and the N(pyrazoles) at 2.030(10) and 2.112(9) Å. One of the nitrate ions is monodentate with a Co–O distance of 2.060(8), the other nitrate is quite symmetrically bidentate coordinated to the cobalt ion with Co–O distances of 2.172(8) and 2.216(8) Å.

The packing of the molecules in the three structures described above is through normal van der Waals forces.

The ddae compounds

Stoichiometries, analytical data, colours and ligand field bands of the compounds obtained with bis(2-(3,5-dimethyl-1-pyrazolyl)ethyl)ethylamine are given in Table 4. The IR spectra of all compounds show the IR pattern which is typical for the ligand ddae, for instance they all contain the characteristic pyrazole peak at about 1560 cm^{-1} The IR spectra also contain bands characteristic for the respective complex anions, viz. the broad band of BF_4^- at *c.* 1100 cm^{-1} and the bands at 1295, 1390, 1475 cm^{-1} for NO_3^-.

The LF spectra of the copper chloride and nitrate compounds showed one very broad absorption band with two distinct maxima (see Table 4), in accordance with the low symmetry environment of the copper ions as a consequence of the distortion from square-pyramidal and the difference in donor strength of the coordinating atoms $N_2N'Cl_2$ and $N_2N'OO'$, respectively (see above).

The LF spectrum of the copper tetrafluoroborate compound shows a less broad absorption band (see Table 4), which might indicate a less distorted environment. The IR spectrum of this compound shows a weak band at 345 cm^{-1}, indicative for an M–F stretching

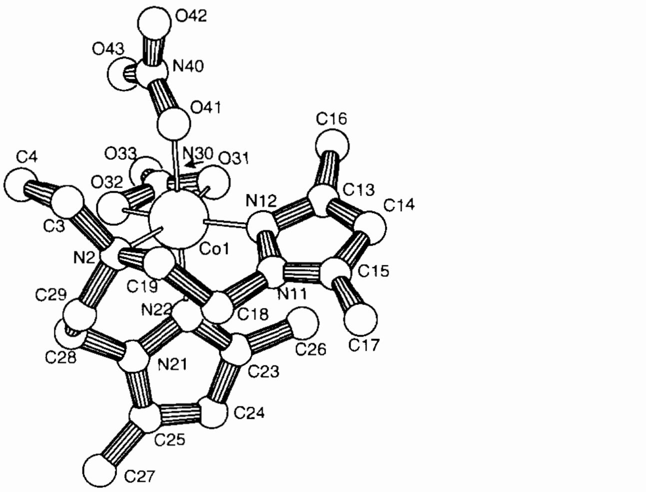

Fig 4 PLUTON [12] projection of $[Co(ddae)(NO_3)_2]$ (**C**), for clarity the H atoms are omitted

TABLE 4. Formula, colour, analytical data and LF maxima for the ddae compounds

Formula	M^{2+} (%) found (calc.)	Colour	M p (°C)	LF maxima^a (10^3 cm^{-1})
$[Co(ddae)(NO_3)_2]^b$	12.1 (12 5)	rose–red	212–213	(21.7)20 2(16.5), 8 7
$[Ni(ddae)(NO_3)_2]^c$	12 1 (12 5)	blue–green	225–226	26.0, 15.9, 8.9
$[Cu(ddae)(Cl)_2]\cdot(C_2H_5OH)$	13.4 (13.5)	green	123–124	13.3(9 1)
$[Cu(ddae)(NO_3)(H_2O)](NO_3)^d$	12.4 (12 8)	light blue	103–105	14.3(8.8)
$[Ni(ddae)(H_2O)(BF_4)_2]$	11.0 (10 9)	green	170–171	26.6, 16.3, 9.0
$[Cu(ddae)(F)(BF_4)]$	14.0 (13 9)	green	>240	15.4

^{a}Values between parentheses denote shoulders on the parent band. ^{b}C, 40 1(40 7), H, 5.96(5.76), N, 20.3(20.8) ^{c}C, 39 8(40.7); H, 5.76(5.76), N, 20.4(20.8) ^{d}C, 39.9(38 8); H, 6.07(5.91), N, 20.1(19 8).

vibration. The latter implies that partial decomposition of BF_4^- has taken place, as also suggested by the analytical data (see Table 4). In this type of compounds the fluoride ion usually bridges between two M^{2+} ions [14, 15], which would be in accord with an N_3F_2 environment for each copper. The phenomenon of BF_4^- decomposition has been reported before for cobalt, nickel and copper tetrafluoroborates, mostly also with pyrazole containing ligands [14, 15].

The LF spectrum of the nickel tetrafluoroborate compound is typical for octahedral coordination with coordinating atoms of varying donor strength. This implies that the BF_4^- ions are coordinated to the Ni^{2+} ion, which is confirmed by the IR spectrum of this compound which shows, apart from the regular BF_4^- absorption bands, an absorption at 770 cm^{-1}, indicative for coordinated fluoroborate [16, 17].

The nickel nitrate compound is isomorphous with the cobalt nitrate compound (*vide infra*) as shown by X-ray powder diffraction. The LF spectra of both compounds are in accord with an octahedral N_3O_3 environment [18, 19].

Attempts to synthesize coordination compounds with a metal to ligand ratio of 1:2 were not successful. Model studies on octahedral $[M(ddae)_2]^{2+}$ species indicate that the methyl substituents on the pyrazole groups of a facial or of a meridional coordinated ddae ligand protrude to such an extent that a second ddae ligand cannot approach the M^{2+} ion. This sterical hindrance is also due to the four-bond chelate bites [3] of ddae, which cause the N–M^{2+}–N coordination angles to be somewhat larger than 90°, thereby pushing the methyl substituents inward. Similar ligands, but with three-bond chelate bites, and consequently small N–M^{2+}–N coordination angles, viz. between about 79° and about 87°, are less hindered by such protruding methyl substituents and may consequently form compounds with a 1:2 metal to ligand ratio, as reported by Schoonhoven *et al.* [20]. Similar ligands with unsubstituted pyrazole groups are of course able to form M:L = 1:2 compounds [6, 21].

Conclusions

The present study has made clear that the ligand bis(2-(3,5-dimethyl-1-pyrazolyl)ethyl)ethylamine readily acts as a tridentate ligand coordinating through the amine nitrogen and the two pyrazole nitrogens both in a facial and in a meridional mode, but sterical factors prevent the formation of 1:2 metal to ligand compounds.

Supplementary material

Tables with the fractional coordinates of the hydrogen atoms, of the non-hydrogen anisotropic thermal parameters, and of the bond lengths and bond angles, and thermal motion ellipsoid plots are available from the authors on request.

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