Synthesis and Co-ordination Chemistry of a Novel Dinucleating Chelating Triazole Ligand. The Crystal Structure of Bis-μ-[4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole-N',μ-N^1,μ-N^2,N'']-bis[aquachloronickel(II)] Dichloride Tetrahydrate †

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Reaction of 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (abpt) with nickel(II) and cobalt(II) salts produces dinuclear co-ordination compounds. One of the compounds, $[Ni_2(abpt)_2Cl_2(H_2O)_2]Cl_2{\cdot}4H_2O$, crystallizes in the triclinic space group $P\bar{1}$ with $a = 6.840(2)$, $b = 10.199(4)$, $c = 12.480(3)$ Å, $\alpha = 78.62(3)$, $\beta = 76.47(2)$, $\gamma = 84.17(3)°$, and $Z = 1$. Refinement based on 4 015 independent reflections yielded a value for R' of 0.034. The dinuclear $Ni_2(abpt)_2$ unit is almost planar. The nickel ions are co-ordinated by four nitrogen atoms with N–Ni–N angles of 93.00(4), 76.74(4), 113.67(4), and 76.47(4)° and Ni–N distances of 2.013(1), 2.029(1), 2.155(1), and 2.164(1) Å. The axial ligands are a water molecule and a chloride ion. The co-ordination of the metal centres is rhombically distorted octahedral. The uncommon ligand-field spectrum is interpreted along with these findings. Variable-temperature magnetic susceptibility measurements for analogous compounds of Ni^{II} and Co^{II} with BF_4^-, Cl^-, or Br^- anions revealed that a relatively weak antiferromagnetic exchange is present in these compounds.

Dinuclear compounds of transition metals form a field of increasing research interest, especially with regard to magnetic exchange. Triazoles are strong nitrogen-donor ligands with several possible co-ordination modes. The co-ordination chemistry of 1,2,3-triazoles has been studied in some detail[1] and these ligands appear to be quite different compared with 1,2,4-triazoles.

Compounds with 1,2- and 2,4-bridging 1,2,4-triazole units have been reported.[2] The 1,2 co-ordination mode can be incorporated in a chelating ligand system by suitable substitutions on the triazole ring, affording interesting stereochemical prospects. To investigate this co-ordination mode we have selected 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole, hereafter abbreviated as abpt (Figure 1). This compound was first synthesized by Dallacker.[3] Geldard and Lions[4] first mentioned it as a potential ligand analogue for terpyridine. However, no further reports on this kind of molecule as a ligand in metal compounds have appeared.

This paper deals with the first results obtained with this ligand. Compositions varied from $M_2(abpt)_2X_4(H_2O)_x$, with M = Ni or Co, X = Cl, Br, or BF_4, and x = 2 or 4. The preparation of these compounds is described and their spectroscopic and magnetic properties are discussed. The crystal structure determination of a nickel compound was undertaken to prove the dinucleating properties of the ligand and for a better understanding of the unusual ligand-field spectra.

Experimental

Starting Materials.—4-Amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole was prepared from hydrazine monohydrate and 2-cyanopyridine.[4] Metal salts were used as commercially available hexahydrates.

Synthesis.—$[Ni_2(abpt)_2Cl_2(H_2O)_2]Cl_2{\cdot}4H_2O$ (1). A solution of abpt (0.7 g, 3 mmol) in warm ethanol (30 cm^3) was added dropwise to a solution of nickel(II) chloride hexahydrate (0.7 g, 3 mmol) in water (15 cm^3). Light blue crystals were formed on standing for several hours. The crystals were isolated by filtration.

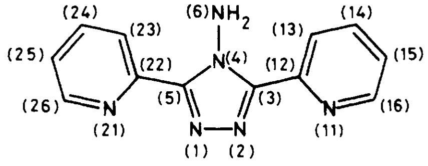

Figure 1. Structural formula and numbering system of 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole

The compounds $[Ni_2(abpt)_2(H_2O)_4][BF_4]_4$ (2), $[Co_2(abpt)_2Cl_2(H_2O)_2]Cl_2{\cdot}4H_2O$ (3), and $[Co_2(abpt)_2Br_2(H_2O)_2]Br_2{\cdot}4H_2O$ (4) were prepared in the same way using 3 mmol metal salt. They precipitated as crystallites or powders, and were isolated by filtration and dried *in vacuo* at room temperature.

Analyses.—The C, H, and N analyses were carried out by Pascher Analytical Laboratory, Bonn, West Germany.

Spectra.—I.r. spectra in the 4 000—180 cm^{-1} region were recorded on a Perkin-Elmer 580B spectrophotometer both for Nujol mulls and CsCl pellets. Ligand-field spectra in the region 28 000—4 000 cm^{-1} were recorded on a Beckman DK-2A UV-VIS spectrophotometer using the diffuse-reflectance method with MgO as a reference.

Magnetic Measurements.—The magnetic susceptibility data were obtained on powdered samples in the temperature region 4—80 K on a PAR model 150A vibrating-sample magnetometer. The observed susceptibilities were fitted by theoretical expressions using least-squares methods. The measurements were corrected for diamagnetism using Pascal constants and for temperature-independent paramagnetism.[5]

X-*Ray Crystallography.*—X-Ray powder data were obtained with a Guinier-type camera using Cu-K_α radiation. A

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† *Supplementary data available* (No. SUP 23996, 19 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Atomic fractional parameters ($\times 10^5$ for Ni, Cl; $\times 10^4$ for O, C, N) of $[Ni_2(abpt)_2Cl_2(H_2O)_2]Cl_2{\cdot}4H_2O$ with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ni	107 336(3)	29 623(2)	2 089(2)	C(16)	6 634(2)	9 263(1)	1 000(1)
N(1)	9 027(2)	4 149(1)	1 222(1)	N(21)	9 733(2)	1 591(1)	1 761(1)
N(2)	8 497(2)	5 477(1)	1 064(1)	C(22)	8 539(2)	2 164(1)	2 606(1)
C(3)	7 325(2)	5 743(1)	1 999(1)	C(23)	7 820(2)	1 439(1)	3 663(1)
N(4)	7 073(2)	4 593(1)	2 769(1)	C(24)	8 371(3)	81(2)	3 878(1)
C(5)	8 173(2)	3 609(1)	2 247(1)	C(25)	9 577(3)	−504(2)	3 036(2)
N(6)	5 972(2)	4 540(1)	3 879(1)	C(26)	10 211(2)	283(1)	1 992(1)
N(11)	7 255(2)	7 971(1)	1 068(1)	Cl(1)	78 480(6)	25 279(4)	−4 612(3)
C(12)	6 566(2)	7 130(1)	2 044(1)	Cl(2)	129 047(6)	25 957(5)	34 024(3)
C(13)	5 272(2)	7 563(1)	2 953(1)	O(1)	13 270(2)	3 195(1)	810(1)
C(14)	4 662(2)	8 913(2)	2 863(1)	O(2)	1 140(3)	5 654(2)	2 911(1)
C(15)	5 339(2)	9 767(1)	1 883(2)	O(3)	1 118(2)	6 699(2)	4 801(1)

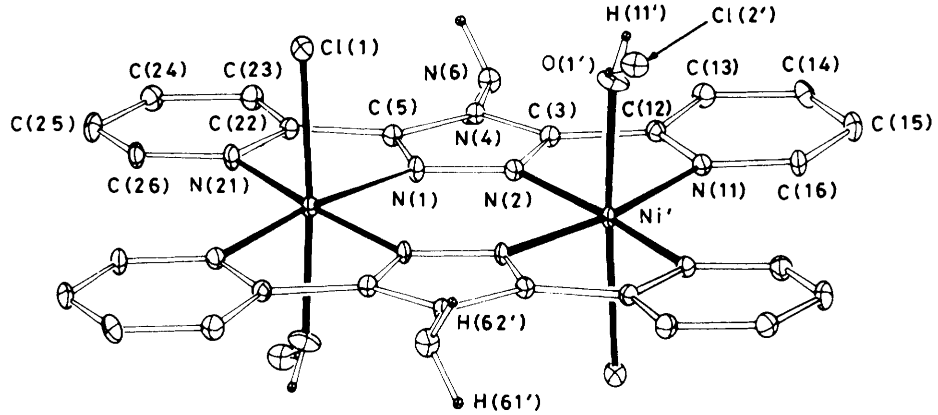

Figure 2. Projection of the structure of $[Ni_2(abpt)_2Cl_2(H_2O)_2]Cl_2{\cdot}4H_2O$ with the atomic labelling system. Lattice water molecules and hydrogen atoms that are bonded to carbon atoms are omitted for clarity. Primed atoms are generated by $2-x$, $1-y$, $-z$

single crystal (0·5 × 0·3 × 0·15 mm) of compound (1) was sealed in a glass capillary.

Crystal data. $C_{24}H_{32}Cl_4N_{12}Ni_2O_6$, $M = 843.80$, triclinic, $a = 6.840(2)$, $b = 10.199(4)$, $c = 12.480(3)$ Å, $\alpha = 78.62(3)$, $\beta = 76.47(3)$, $\gamma = 84.17(3)°$, $U = 828.44$ Å^3 (cell used in the refinement), $a = 10.199(4)$, $b = 6.840(2)$, $c = 12.752(3)$ Å, $\alpha = 107.91(3)$, $\beta = 97.97(3)$, $\gamma = 95.83(3)°$ (reduced cell), space group $P\bar{1}$, $D_m = 1.67$ Mg m^{-3}, $Z = 1$, $D_c = 1.69$ Mg m^{-3}, μ(Mo-K_α) = 15.24 cm^{-1}, λ(Mo-K_α) = 0·709 30 Å, $F(000) = 432$.

Data collection and processing. A CAD4 diffractometer with graphite-monochromated Mo-K_α radiation was employed. 4 826 Independent reflections were measured ($2 < \theta < 30°$), 4 015 with $I > 2\sigma(I)$. The data were corrected for Lorentz, polarization, absorption,[6] and extinction.

Solution and refinement of the structure. Scattering factors were taken from ref. 7. A three-dimensional Patterson synthesis revealed the positions of the nickel and chlorine atoms. The positions for the other atoms were found by the usual Fourier (difference) techniques and refined by least squares. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were refined isotropically. Several cycles of refinement led finally to $R = \Sigma|\Delta F|/\Sigma F_o = 0.022$; $R' = [\Sigma w(\Delta F)^2/\Sigma w F_o^2]^{\frac{1}{2}} = 0.034$. The weighting scheme was $w = 1/\sigma_F^2$. The final Fourier difference map revealed 21 small but significant peaks. Sixteen of these peaks were located on the bonds in the rings of the ligand and are attributed to bonding electrons. No further attempts were made to assign the remaining peaks. The atomic fractional parameters for the non-hydrogen atoms are in Table 1. Local programs[6] were used on Amdahl and IBM computers.

Results and Discussion

X-*Ray structure of* $[Ni_2(abpt)_2Cl_2(H_2O)_2]Cl_2{\cdot}4H_2O$.— The crystal structure consists of $[Ni_2(abpt)_2Cl_2(H_2O)_2]^{2+}$ cations, two Cl^- anions, and four lattice water molecules, held together by hydrogen bridges. There is an inversion centre at the centre of the cation. A projection of the structure is presented in Figure 2, together with the atomic labelling system; lattice water molecules O(2) and O(3) are omitted for clarity. Relevant interatomic distances and angles are in Table 2.

The $[Ni_2(abpt)_2]^{4+}$ system is nearly planar. The distance of the nickel atoms to the least-squares plane through the ligand is 0.07 Å. In this plane the nickel atoms are linked by two triazoles *via* their N(1)–N(2) bridging mode. The equatorial co-ordination is completed by the two pyridine nitrogens. The nickel–triazole nitrogen bonds are shorter than the nickel–pyridine nitrogen bond. The planarity of the ligand is not unexpected because it is a conjugated system. In the free ligand the angles N(2)–C(3)–C(12) and N(4)–C(3)–C(12) determining the position of the pyridine group would be expected to be about 126°. On complexation certain deformations occur in the structure of the ligand to obtain a co-ordination around the metal centres that does not differ too much from octahedral. The angle N(2)–C(3)–C(12) is much smaller [118.4(1)°] than N(4)–C(3)–C(12) [132.5(1)°] and

Table 2. Relevant interatomic distances (10^{-10} m) and angles (°) for $[Ni_2(abpt)_2Cl_2(H_2O)_2]Cl_2\cdot4H_2O$ with estimated standard deviations in parentheses *

Ni–Ni′	4.134 8(3)	H(16)–H(26)	2.19(3)	C(16)–N(11)	1.336(2)	C(16)–H(16)	1.01(2)
Ni–Ni″	6.364 8(3)	N(1)–N(2)	1.354(1)	C(5)–C(22)	1.467(2)	C(23)–H(23)	0.97(2)
Ni–N(1)	2.013(1)	N(2)–C(3)	1.312(2)	N(21)–C(22)	1.365(2)	C(24)–H(24)	0.86(2)
Ni–N(2)	2.029(1)	C(3)–N(4)	1.359(2)	C(22)–C(23)	1.384(3)	C(25)–H(25)	0.77(3)
Ni–N(11)	2.155(1)	N(4)–C(5)	1.369(2)	C(23)–C(24)	1.388(2)	C(26)–H(26)	0.97(2)
Ni–N(21)	2.164(1)	C(5)–N(1)	1.311(2)	C(24)–C(25)	1.373(3)	O(1)–H(11)	0.73(3)
Ni–O(1)	2.096(1)	N(4)–N(6)	1.408(2)	C(25)–C(26)	1.387(2)	O(1)–H(12)	0.67(3)
Ni–Cl(1)	2.426 6(4)	C(3)–C(12)	1.463(2)	C(26)–N(21)	1.332(2)	O(2)–H(21)	0.78(4)
N(1)–N(21)	2.588(2)	N(11)–C(12)	1.358(2)	N(6)–H(61)	0.94(2)	O(2)–H(22)	0.68(4)
N(2)–N(11)	2.599(2)	C(12)–C(13)	1.384(2)	N(6)–H(62)	0.88(2)	O(3)–H(31)	0.65(3)
N(1)–N(2′)	2.932(2)	C(13)–C(14)	1.388(2)	C(13)–H(13)	0.89(2)	O(3)–H(32)	0.94(3)
N(11)–N(21′)	3.616(2)	C(14)–C(15)	1.366(2)	C(14)–H(14)	0.98(2)		
C(16)–C(26)	3.817(2)	C(15)–C(16)	1.391(2)	C(15)–H(15)	0.88(2)		

N(1)–Ni–N(2′)	93.00(4)	C(3)–N(4)–C(5)	105.8(1)	N(1)–C(5)–C(22)	118.1(1)
N(1)–Ni–N(21)	76.47(4)	N(4)–C(5)–N(1)	108.5(1)	N(4)–C(5)–C(22)	133.4(1)
N(2)–Ni–N(11)	76.74(4)	C(5)–N(1)–N(2)	108.6(1)	C(5)–C(22)–N(21)	111.5(1)
N(11′)–Ni–N(21)	113.67(4)	C(3)–N(4)–N(6)	123.6(1)	C(5)–C(22)–C(23)	125.9(1)
Ni–N(1)–N(2)	132.63(8)	C(5)–N(4)–N(6)	130.5(1)	N(21)–C(22)–C(23)	122.6(1)
Ni–N(1)–C(5)	118.80(9)	N(2)–C(3)–C(12)	118.4(1)	C(22)–C(23)–C(24)	118.6(1)
Ni′–N(2)–N(1)	134.22(8)	N(4)–C(3)–C(12)	132.5(1)	C(23)–C(24)–C(25)	119.3(1)
Ni′–N(2)–C(3)	117.67(9)	C(3)–C(12)–N(11)	112.1(1)	C(24)–C(25)–C(26)	118.8(1)
Ni′–N(11)–C(12)	115.05(8)	C(3)–C(12)–C(13)	125.3(1)	C(25)–C(26)–N(21)	123.5(1)
Ni′–N(11)–C(16)	127.4(1)	N(11)–C(12)–C(13)	122.6(1)	C(26)–N(21)–C(22)	117.2(1)
Ni–N(21)–C(22)	115.08(8)	C(12)–C(13)–C(14)	118.6(1)	H(61)–N(6)–H(62)	115(2)
Ni–N(21)–C(26)	127.6(1)	C(13)–C(14)–C(15)	119.3(1)	H(11)–O(1)–H(12)	106(3)
Cl(1)–Ni–O(1)	176.07(4)	C(14)–C(15)–C(16)	119.2(1)	H(21)–O(2)–H(22)	80(4)
N(1)–N(2)–C(3)	108.0(1)	C(15)–C(16)–N(11)	122.8(1)	H(31)–O(3)–H(32)	108(3)
N(2)–C(3)–N(4)	109.2(1)	C(16)–N(11)–C(12)	117.6(1)		

* Primed atoms are generated by $2 - x$, $1 - y$, $-z$, double primed atoms by $2 - x$, $-y$, $-z$.

Table 3. Interatomic distances (Å) and angles (°) for the hydrogen bridges in $[Ni_2(abpt)_2Cl_2(H_2O)_2]Cl_2\cdot4H_2O$ with estimated standard deviations in parentheses *

Cl(1) ··· O(1′)	3.233(1)	Cl(1) ··· H(11′) ··· O(1′)	165(3)
Cl(1‴) ··· O(2)	3.209(2)	Cl(1‴) ··· H(21) ··· O(2)	152(3)
Cl(2) ··· O(1)	3.126(2)	Cl(2) ··· H(12) ··· O(1)	164(3)
Cl(2″) ··· O(3)	3.234(2)	Cl(2″) ··· H(32) ··· O(3)	172(2)
Cl(2′) ··· N(6)	3.253(2)	Cl(2′) ··· H(61) ··· N(6)	158(1)
O(2) ··· O(3)	2.771(2)	O(2) ··· H(31) ··· O(3)	147(4)
O(3″) ··· N(6)	2.911(2)	O(3″) ··· H(62) ··· N(6)	166(2)

* Primed atoms are generated by $x - 1$, y, z, double primed atoms by $1 - x$, $1 - y$, $1 - z$, and triple primed atoms by $1 - x$, $1 - y$, $-z$.

Table 4. Ligand-field transitions (10^3 cm^{-1}) for $M_2(abpt)_2X_2(H_2O)_x$, with M = Ni or Co, X = Cl, Br or BF_4, and x = 2 or 4. Assignments are based on D_{4h} symmetry

Compound			Compound		
(1)	(2)	Assignment	(3)	(4)	Assignment
26.7	26.7	[a]	27.8	27.8	[a]
17.4	17.4	$^2E_g \leftarrow {}^3B_{1g}$	20.0	20.0	$^4A_{2g} \leftarrow {}^4A_{2g}$(br)
12.9 [b]	13.3 [b]	$^3A_{2g} \leftarrow {}^3B_{1g}$			
11.7	11.8	$^3B_{2g}(T_{2g})$, ^3E_g[c]$(T_{2g}) \leftarrow {}^3B_{1g}$	10.1	10.2	$^4E_g \leftarrow {}^4A_{2g}$
8.5	8.6	^3E_g[c]$(T_{2g}) \leftarrow {}^3B_{1g}$	7.1	7.1	$^4B_{2g} \leftarrow {}^4A_{2g}$

[a] Shoulder on charge-transfer band. [b] Shoulder. [c] Rhombic splitting of $^3E_g(T_{2g})$.

C(3)–C(12)–N(11) [112.1(1)°] is smaller than C(3)–C(12)–C(13) [125.3(1)°]. No further deformations seem to occur as a result of the strain in the system. The distance between the opposite pyridyl hydrogen atoms H(16)–H(26) is 2.19(3) Å, which is about the van der Waals contact.[8] The variation in the Ni–N distances (0.15 Å) is quite large.

The packing of cations and anions in the unit cell is depicted in Figure 3. The distance between the ligand planes is 6.3 Å. The units are linked by hydrogen bridges involving all water hydrogens except H(22) and the two hydrogens of the amino-group (Table 3). The complex system with seven different hydrogen bridges incorporates the two chlorine ions and thus binds the units together. The structure may be compared to that of $[NiL(H_2O)_2]_2Cl_4\cdot2H_2O$,[9] L = 1,4-dihydrazinophthalazine, which has a similar framework, in which two ligands link the two metals together with a central dinucleating part containing two nitrogen atoms.

The essential difference between the two structures, however, is that the central part is a five-membered ring in the present compound and a six-membered one in the phthalazine compound. Therefore, the two terminal N atoms are in line with the two central nitrogen atoms in the phthalazine compound, and no deformation is required to obtain a symmetric co-ordination of the nitrogen atoms around the metal centres.

Spectra.—The i.r. spectra of the four compounds are all very similar, with respect to band positions and relative intensities, apart from the absorptions originating from the BF_4 anion. This indicates that the dinuclear structure of (1) must also be present in the other three compounds.

For the nickel compounds additional evidence for identical structures comes from the ligand-field spectra that are much alike (Table 4). The rhombic distortion of the D_{4h} spectrum is clearly reflected in the ligand-field spectra. The bands at about 12 000 and 8 600 cm^{-1} for the nickel(II) compounds are split components of the $^3E_g(^3T_{2g})$ level. No attempts were undertaken to determine ligand-field parameters due to the uncertainty in the assignment.

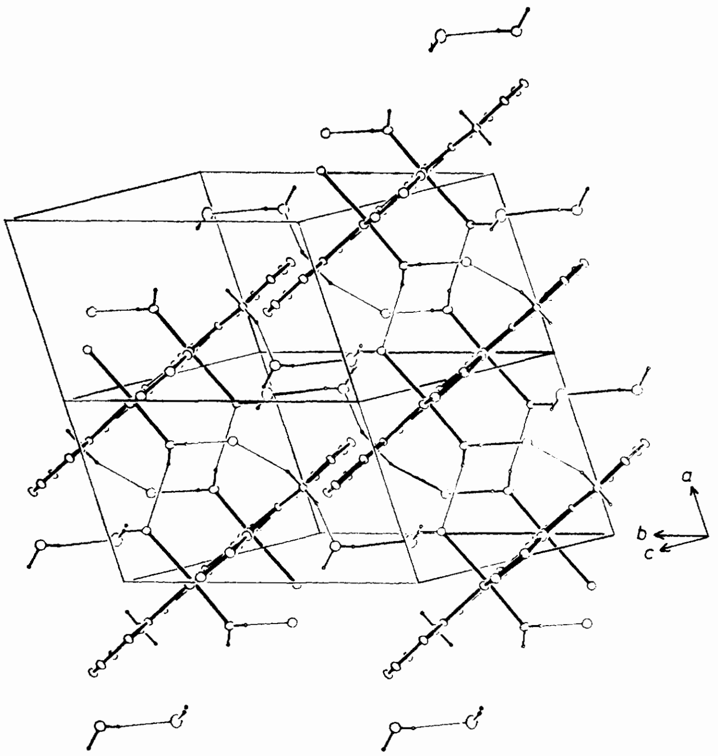

Figure 3. The unit-cell packing of $[Ni_2(abpt)_2Cl_2(H_2O)_2]Cl_2{\cdot}4H_2O$. The hydrogen atoms that are bonded to carbon atoms are omitted for clarity

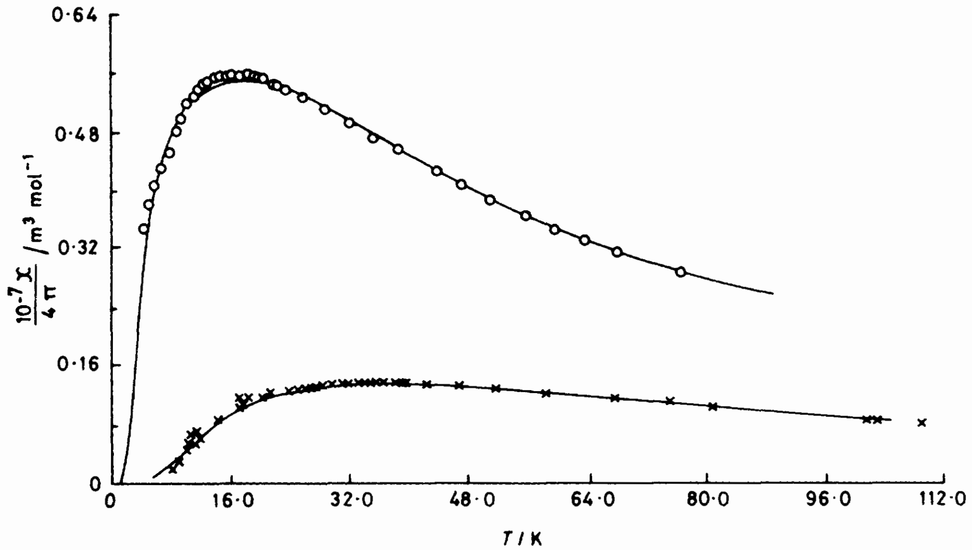

Figure 4. Magnetic susceptibility per metal ion *vs.* temperature curves for $[Ni_2(abpt)_2Cl_2(H_2O)_2]Cl_2{\cdot}4H_2O$ (×) and $[Co_2(abpt)Cl_2(H_2O)_2]Cl_2{\cdot}4H_2O$ (○). The solid lines represent the least-squares fit of the data to the theoretical equations given in the text

The cobalt compounds have the same *X*-ray powder pattern as the nickel chloride compound. Therefore it is justified to assign the dinuclear structure also to the former.

Magnetic Measurements.—For polynuclear structures the exchange coupling between the metal centres is usually investigated by magnetic susceptibility measurements. Comparison of the magnetic exchange of different compounds may give information about the magnitude of the exchange and the possible exchange mechanism. In the present study, magnetic susceptibilities have been measured from 4 to 80 K.

The exchange in polynuclear units is usually expressed in terms of the exchange coupling constant J. For dinuclear species the Hamiltonian is $H = -2JS_1S_2$, at least when only exchange between nearest neighbours is considered. From this Hamiltonian the magnetic susceptibility χ can be derived. For Ni^{II}, $S_1 = S_2 = 1$ yields equation (i) in which N, β, and k are fundamental constants, g and J are adjustable parameters,[5] and $x = J/kT$. The obtained parameters were fitted by a more

$$\chi = \frac{Ng^2\beta^2}{kT}\left(\frac{5 + e^{4x}}{5 + 3e^{4x} + e^{6x}}\right) \qquad \text{(i)}$$

Table 5. Magnetic parameters for $M_2(abpt)_2X_4(H_2O)_x$, with M = Ni or Co, X = Cl, Br, or BF_4 and x = 2 or 4 with estimated standard deviations in parentheses

Compound	$-J$/cm^{-1}	g	zJ'/cm^{-1}	$-D$/cm^{-1}
(1)	12.5(2)	2.15(1)	2.3(2)	10(4)
(2)	9.0(2)	2.25(1)	0.0	25(9)
(3)	4.0(1)	2.42(1)		
(4)	4.2(1)	2.34(1)		

detailed formula of Ginsberg[10] that includes interdimer exchange (zJ') and zero field splitting (D). The results are listed in Table 5, and illustrated in Figure 4, for compounds (1) and (3).

For Co^{II}, $S_1 = S_2 = \frac{3}{2}$ and the appropriate formula is (ii).

$$\chi = \frac{Ng^2\beta^2}{kT}\left(\frac{14 + 5e^{6x} + e^{10x}}{7 + 5e^{6x} + 3e^{10x} + e^{12x}}\right) \qquad \text{(ii)}$$

As the orbital moment is only partly quenched for Co^{II}, this formula cannot be entirely correct. Using an effective spin $S_{eff.} = \frac{1}{2}$ to approximate the exact low-temperature state of the Co^{II}, however, resulted in less good fits in this case.

When magnetic data are fitted by least-squares methods the obtained parameters usually have small standard deviations. However, when comparing J values for different compounds a difference of >10% can be considered as significant.[11] Magnetic exchange in a series of nickel dimers with N–N bridges has been studied in only a limited number of compounds.[12] The J values appeared to increase when the electron overlap population of the π molecular orbitals of the bridging system increases. Ball and Blake[12] concluded therefore that an important part of the superexchange takes place *via* the π electrons of the ligand.

Our results indicate that the exchange in the present nickel compounds is not much different from that of 3,5-bis-(pyridin-2-yl)pyrazolate. However, the π-bonding properties are significantly different for pyrazoles and triazoles.[13] Therefore, the observed magnetic exchange cannot only originate from the π-electron exchange. Recent observations by Kahn,[14] Hodgson, Hendrickson, and Hatfield[15,16] have shown that magnetic exchange through σ electrons is very important. Therefore, bond lengths and metal–ligand–metal bond angles should also be taken into account in quantitative discussions about magnetic exchange–structure correlations. More compounds of closely related, but significantly different, structures will be needed together with detailed magnetic studies for a better understanding of magnetic superexchange in this type of compound.

Conclusions

The results described in this paper have shown that 4-substituted 3,5-bis(pyridin-2-yl)-1,2,4-triazoles are interesting dinucleating chelating ligands. The dinuclear transition-metal compounds formed are interesting from the point of view of magnetochemistry but also from their ligand-field spectra, because of the irregular geometry and steric strain induced by the ligand. Forthcoming investigations will deal with studies of related ligands and with spectroscopic and magnetic studies of these compounds, to allow a detailed study of structure–magnetism correlations.

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References

1 B. J. Graves and D. J. Hodgson, *Inorg. Chem.*, 1981, **20**, 2223 and refs. therein.
2 D. W. Engelfriet, W. L. Groeneveld, and G. M. Nap, *Z. Naturforsch., Teil A*, 1980, **35**, 1382; G. Vos, J. G. Haasnoot, and W. L. Groeneveld, *Z. Naturforsch., Teil B*, 1981, **36**, 802.
3 F. Dallacker, *Monatsh. Chem.*, 1960, **91**, 294.
4 J. F. Geldard and F. Lions, *J. Org. Chem.*, 1965, **30**, 318.
5 A. Earnshaw, 'Introduction to Magnetochemistry,' Academic Press, London, 1968.
6 R. A. G. de Graaff, *Acta Crystallogr., Sect. A*, 1973, **29**, 298.
7 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
8 'Handbook of Chemistry and Physics,' CRC Press, Boca Raton, Florida, 1979, vol. 60.
9 J. E. Andrew and A. B. Blake, *J. Chem. Soc. A*, 1969, 1408.
10 A. P. Ginsberg, *Inorg. Chem.*, 1972, **11**, 2884.
11 J. Reedijk and R. W. M. ten Hoedt, *Recl. Trav. Chim. Pays-Bas*, 1982, **101**, 49 and refs. therein.
12 P. W. Ball and A. B. Blake, *J. Chem. Soc. A*, 1969, 1415.
13 K. T. Potts, *Chem. Rev.*, 1961, **61**, 87.
14 O. Kahn, *Inorg. Chim. Acta*, 1982, **62**, 3.
15 M. S. Haddad, S. R. Wilson, D. J. Hodgson, and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1981, **103**, 384.
16 V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, 1976, **15**, 2107.

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