Synthesis and Crystal and Molecular Structure of a Tetranuclear 'Pair-of-dimers' Nickel(II) Schiff Base Complex. Magnetism of the Cu4 Analogue

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Newly designed 'pair-of-dimers' complexes of Ni^{II} and Cu^{II} have been synthesized by linking together two binuclear metal Schiff base moieties with an exogenous μ-di-3,5-dimethylpyrazolate bridge; antiferromagnetism in the Cu_4^{II} complex involves interaction between the coupled binuclear fragments but probably of an *inter-* rather than *intra*-molecular nature.

There has been rapid growth in recent reports of the synthesis of new tetranuclear transition metal complexes. A variety of core shapes have been obtained such as cubanes,[1,2] adamantanes,[3] squares,[4] rhombuses[5] and butterfly-wings.[6] Some of these have been obtained by chance rather than by design. The main impetus for such work has been the proposed existence of a spin-coupled Mn_4 tetranuclear centre, possibly incorporating oxo/hydroxo bridging groups, in the manganese site of the photosynthetic water oxidation centre (WOC).[7,8] While a number of Mn_4 model compounds have been reported,[1,2,6] the confirmation of a newly designed tetranuclear structures is often more readily achieved using Ni_4^{II} or Cu_4^{II} analogues, the magnetic and bioinorganic properties of which are interesting in their own right. We have been
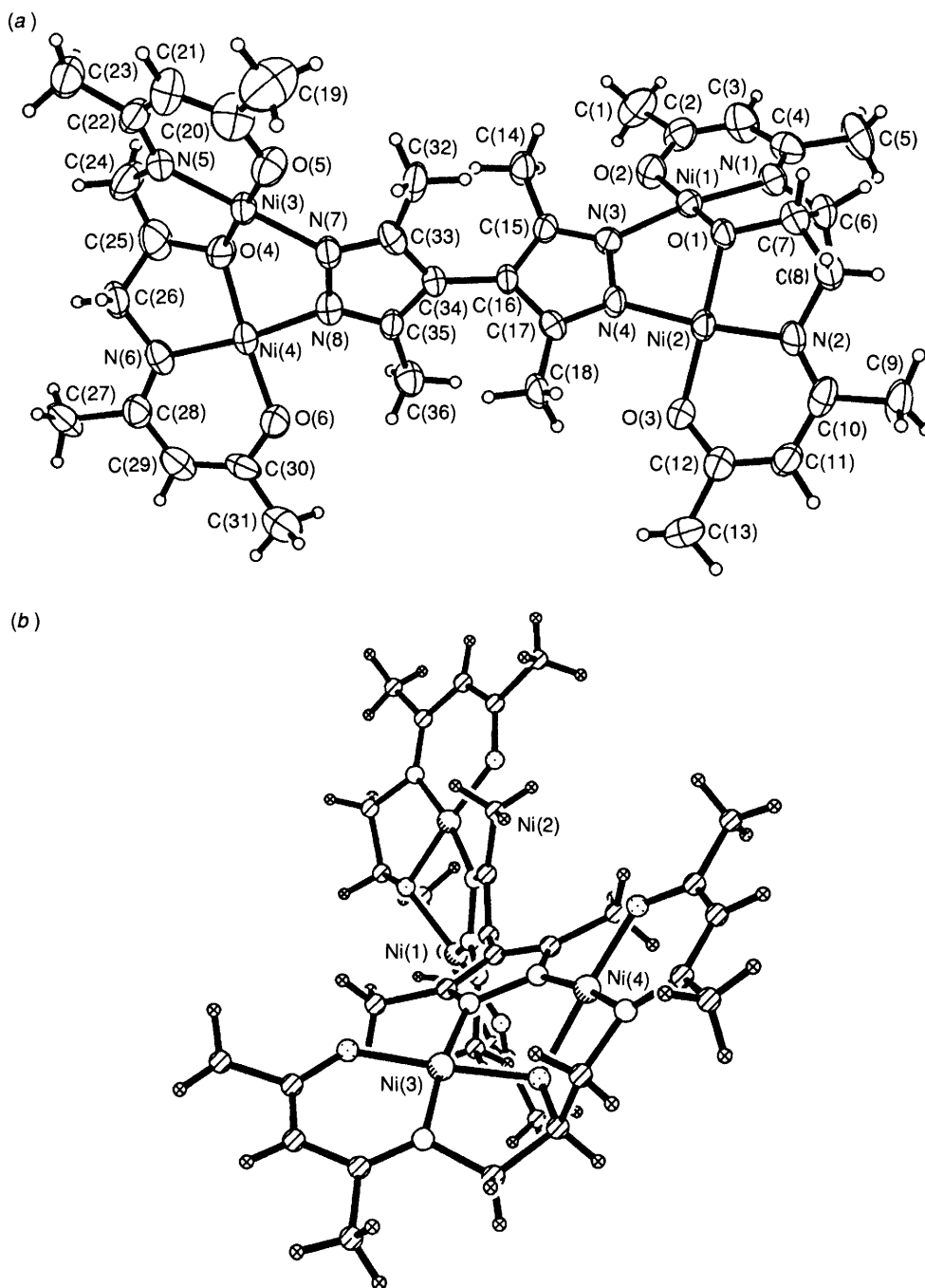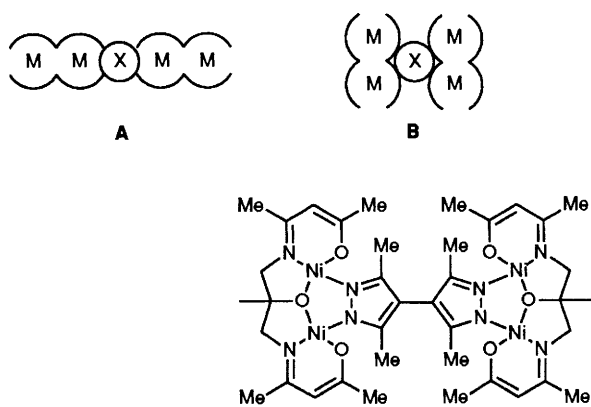
Fig. 1 Molecular structure and numbering scheme for [(LNi$_2$)$_2$(mdpz)] viewed from above (a) and from the side (b). Pertinent bond lengths (Å) and angles (°): Ni(1)–O(1) 1.862(7), Ni(1)–N(1) 1.848(7), Ni(1)–O(2) 1.818(8), Ni(1)–N(3) 1.887(6), Ni(2)–O(1) 1.851(6), Ni(2)–O(3) 1.811(7), Ni(2)–N(2) 1.867(8), Ni(2)–N(4) 1.913(7), Ni(1)···Ni(2) 3.013(2), Ni(3)···Ni(4) 3.062(2), Ni(1)–O(1)–Ni(2) 108.5(3), Ni(3)–O(4)–Ni(4) 111.5(4). Torsion angle C(15), C(16)/C(33), C(44) 58.8. See text for other Ni···Ni contacts.

concentrating on the less well studied pair-of-dimer design.[9,10] In our approach an organic spacer moiety (X) is incorporated into a tetranucleating or a double-binucleating framework of the linear **A** or rectangular **B** types shown below.

The magnetic exchange properties of the M···M 'pairs' have been well established in the parent binuclear complexes[11] and it remains to be seen how the degree of coupling, if any, across the X spacer is related to size, degree of conjugation, donor atom, etc. From the biomodelling point of view it is possible to conceive of the spacer and its binucleating 'arms' as appropriate amino acid residues which, in the case of the WOC, should be chiefly O- and N-donor atoms.[7,8] Future scope for

these kinds of small exchange-coupled clusters also includes the design and synthesis of polymeric molecular magnetic materials.[12]

In the present study a type **B** framework has been successfully obtained by using an exogenous di-μ-3,5-dimethylpyrazolate bridging group to hold together two binuclear Schiff base Ni$_2$ or Cu$_2$ complexes. Thus, the *in situ* reaction of N,N'-(2-hydroxypropylene)bis(acetylacetone-imine) (LH$_3$),[11] 4,4'-di-3,5-dimethylpyrazole (mdpz),[13] MX$_2$ salt and KOH in methanol, in 2:1:4:8 ratio, yielded red–brown or blue crystals, respectively, of the [(LNi$_2$)$_2$(mdpz)] and [(LCu$_2$)$_2$(mdpz)] complexes. These com-

Fig. 2 Plot of χ_{Cu} vs. T/K for $[(LCu_2)_2(mdpz)]$. The solid line is that calculated using a tetranuclear model with J_1 (i.e. $J_{Cu\cdots Cu}$) $-138\,cm^{-1}$; J_2 $-79\,cm^{-1}$; $g = 2.00$; $N\alpha = 60 \times 10^{-6}\,cm^3\,mol^{-1}$; fraction monomer $= 0.02$ (other cross-coupling J values set at zero; see text).

pounds were characterized by elemental analyses and spectroscopic methods (IR, UV–VIS, ^{1}H and ^{13}C NMR). The ^{13}C NMR spectrum at 300 MHz of a CDCl$_3$ solution of the diamagnetic nickel complex was well resolved and showed interesting features. Five CH_3 resonance lines were observed with shifts δ 11.31, 11.53, 20.32, 23.21 and 23.23. The methyl group carbons of the bridging dipyrazolate ligand (δ 11.31 and 11.53), therefore, fall into two sets of two as do the ring carbon to which they are attached (δ 148.48 and 149.05). If it is assumed that the molecular structure in the solid state (vide infra) is retained in solution, these different carbon environments probably occur because of a combination of restricted rotation about C(16)–C(34), conformational differences in the LNi$_2$ group attached to each pyrazole ring and of the tilting of one LNi$_2$ (pyrazole)-group relative to the other. The effect becomes less noticeable further away from the C(16)–C(34) centre, as anticipated, but is nevertheless detectable. Thus, the CH_3CO methyl carbon resonances are separated by a few Hz and observed as two lines at δ 23.21 and 23.23, as are the methine carbon such as C(3) at δ 99.68 and 99.70. The other outer methyl $CH_3C=N$ resonance at δ 20.32 cannot be resolved further. ^{1}H NMR and ^{13}C–^{1}H correlation spectra are consistent with these observations and assignments.

The molecular structure† of $[(LNi_2)_2(mdpz)]$ is viewed from two directions in Fig. 1. It confirms the desired pair-of-dimers structure and displays clear twisting around the central C(16)–C(34) bond brought about by interaction of the 3,3′ and 5,5′ methyl groups on the pyrazoles. The torsion angle between C(15)–C(16) and C(33)–C(34) is 58.8°. The C(16)–C(34) bond lengths of 1.48(1) Å is indicative of a single bond and can be compared with a double bond in a related binuclear Ni$_2$ macrocyclic complex (1.34 Å),[14] a partial double bond in a Fe$_2$ compound (1.41 Å)[15] and a single bond in a Cu$_2$ complex containing the tetraacetylethanate bridge (1.51 Å).[16] Thus, there is no conjugation between the two pyrazole rings of the present compound but there is delocalization within each ring. Each *trans*-NiN$_2$O$_2$ chromophore is square-planar and the two coordination planes within each (LNi$_2$)$^+$ moiety are not coplanar because of the pyramidal nature of O(1) and O(4) (solid angles of 334 and 342°, respectively). These endogenous bridging oxygen atoms are up and down in relation to each other. The Ni$\cdots$Ni distances are not the same within each (LNi$_2$)$^+$ group i.e. Ni(1)–Ni(2) 3.013(2); Ni(3)–Ni(4) 3.062(2)
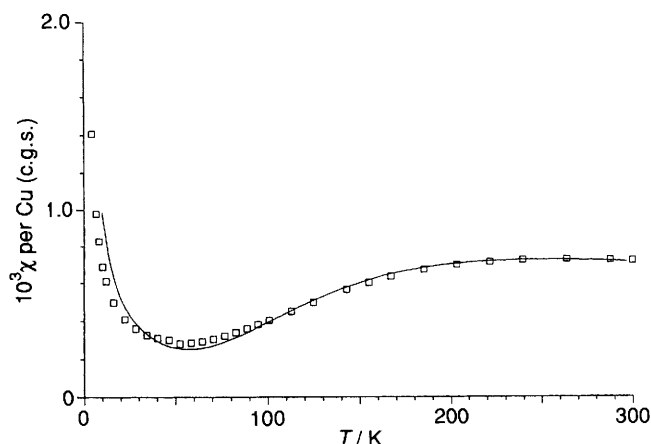
Å. Owing to the twisting around the central C(16)–C(34) linkage the four Ni atoms are not disposed in a flat rectangular array; see Fig. 1. Thus, Ni(1)–Ni(3) 9.123(2), Ni(1)–Ni(4) > 9.5, Ni(2)–Ni(3) 9.407(2) and Ni(2)–Ni(4) 9.324(2) Å. The intermolecular Ni$\cdots$Ni contact distances are, in fact, closer than are the intramolecular ones. Some of these include Ni(1)–Ni(1′) 5.319(3), Ni(2)–Ni(1′) 6.351(2), Ni(4)–Ni(4′) 5.187(3) and Ni(3)–Ni(4′) 5.977(2) Å. No obvious acetylacetonato O atom bridges of the type O–Ni$\cdots$O–Ni can be discerned from the packing diagram.

Microanalytical and IR data on the $[(LCu_2)_2(mdpz)]$ complex show that it contains one H$_2$O molecule per tetranuclear moiety. Crystals suitable for X-ray diffraction study have not been obtained to date, but a powder diffractogram shows that it is not isostructural with the Ni$_4$ complex. Variable-temperature magnetic susceptibility data in the range 295–4.2 K clearly show the occurrence of a broad maximum at ca. 260 K indicative of antiferromagnetic coupling. An increase in χ_{Cu} occurs at low temperatures due to the ubiquitous monomer impurity. Corresponding μ_{Cu} values vary from 1.3 μ_B at 295 K to 0.2 μ_B at 4.2 K. The magnetic behaviour is actually quite similar to that recently reported by Thompson et al.[10] for a flat rectangular (pair of dimers) Cu$_4$ system bridged by a planar aromatic bis(diazene) fragment. These workers ascribed a significant component of the observed antiferromagnetic coupling to *intra*molecular coupling across the planar bridging unit. While further work is required in the present case, particularly in regard to knowledge of the precise molecular structure, we believe that *inter*molecular coupling to adjacent molecules is likely to be important in view of the structural data obtained on the Ni$_4$ complex and of the recent report of intermolecular effects occurring in a Cu$_2$ system containing a related bridging unit to that used here.[16] Certainly, we have found that the use of a two J model,[17] rather than a single J isolated-dimer model, is required to fit the χ_{Cu}/T data. The J_1 value noted in Fig. 2, assigned to the LCu$_2$ fragment, is similar in size and sign to that observed in the parent binuclear systems, but the shape of the susceptibility plot in the χ_{max} region is different in the present compound because of the extra coupling parameter.

Finally, we note that molecular designs of the present type allow the possibility of preparing mixed-metal/mixed-ligand species such as $[(LM_2)(mdpz)(L'M'_2)]$. The Mn^{III} derivative of the present ligand combination has also been obtained, and is being characterized.

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† Crystal data for $[(LNi_2)_2(mdpz)](Ni_4C_{36}H_{50}N_8O_6)$: trigonal, $R\bar{3}$, $a = b = c = 19.770(3)$ Å, $\alpha = \beta = \gamma = 101.05\,(1)°$, $V = 7231\,(2)$ Å^3, $Z = 6$, $D_c = 1.28$, $D_m = 1.29(1)$ g cm^{-3}. Structure solution and refinement based on 3940 reflections with $I \geqslant 3\sigma\,(I_o)$ converged at a residual of 0.07. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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