

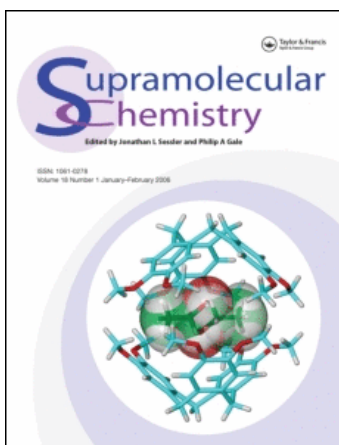
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### Synthesis and Structures of 3,5-disubstituted 1,2,4-triazole Head Units and Incorporation of 3,5-dibenzoyl-1,2,4-triazolate into New [2 + 2] Schiff-Base Macrocyclic Complexes

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# Synthesis and Structures of 3,5-disubstituted 1,2,4-triazole Head Units and Incorporation of 3,5-dibenzoyl-1,2,4-triazolate into New [2 + 2] Schiff-Base Macrocylic Complexes

CARSTEN D. BRANDT<sup>a</sup>, JONATHAN A. KITCHEN<sup>a</sup>, UDO BECKMANN<sup>a</sup>, NICHOLAS G. WHITE<sup>a</sup>, GEOFFREY B. JAMESON<sup>b</sup> and SALLY BROOKER<sup>a,\*</sup>

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The synthesis and characterization of sodium 3,5-diacetyl-1,2,4-triazolate ( $4^{\text{Me}}$ ) and sodium 3,5-dibenzoyl-1,2,4-triazolate ( $4^{\text{Ph}}$ ), both of which can be used as head unit building blocks in Schiff-base reactions, are reported. The crystal structures of sodium 3,5-diacetyl-1,2,4-triazolate, as  $[4^{\text{Me}}(\text{H}_2\text{O})]_{\infty}$ , and sodium 3,5-dibenzoyl-1,2,4-triazolate, as  $[4^{\text{Ph}}(\text{CH}_3\text{OH})_2]_2$ , have been determined. The former is a helical polymer whilst the latter is a methanol-bridged dimer. The lead(II) templated cyclization reaction of sodium 3,5-dibenzoyl-1,2,4-triazolate ( $4^{\text{Ph}}$ ) with 1,3-diaminopropane or 1,4-diaminobutane, respectively, leads to the formation of two new [2 + 2] Schiff-base macrocycles as their lead(II) complexes,  $[\text{Pb}_2\text{L}^{3\text{Ph}}(\mu\text{-OH})]\text{ClO}_4$  (5) and  $[\text{Pb}_2\text{L}^{4\text{Ph}}(\mu\text{-OH})]\text{ClO}_4$  (6), respectively. Transmetalation of 5 with nickel(II) ions yields a novel, structurally characterized, dinickel(II) macrocyclic complex,  $[\text{Ni}_2\text{L}^{3\text{Ph}}(\text{NCS})_2]$  (7), which features double triazolate bridging of the two five-coordinate nickel(II) ions.

**Keywords:** Triazole; Macrocyclic; Structure; Sodium; Nickel

## INTRODUCTION

The incorporation of 1,2,4-triazole moieties into Schiff-base macrocycles is of considerable current interest as complexes of 1,2,4-triazoles are being developed for potential use in applications such as magnetic materials [1,2] and photochemically driven molecular devices [3]. The incorporation of such moieties into a macrocyclic framework will result in

greater stability and control of nuclearity, bridging and metal ion environment (donors, geometry etc) [1,4,5]. Torres and co-workers have successfully isolated some triazolate-containing macrocyclic complexes but none of them have been structurally characterized to date [6,7]. Alcade *et al.* were able to isolate and structurally characterize some metal-free triazolate-containing macrocycles, however no metal complexes have been reported to date [8]. In contrast, the Schiff-base macrocycles  $(\text{L}^{3\text{Me}})^{2-}$  and  $(\text{L}^{4\text{Me}})^{2-}$  (Fig. 1), which we have obtained from the lead(II) templated [2 + 2] condensation of sodium (or potassium) 3,5-diacetyl-1,2,4-triazolate and 1,3-diaminopropane or 1,4-diaminobutane, respectively, have facilitated the preparation and structural characterization of a range of interesting cobalt(II), cobalt(III) and copper(II) complexes [1, 9–11]. However, the use of 3,5-diacetyl-1,2,4-triazolate as the head unit in these Schiff-base macrocycles resulted in several synthetic challenges/difficulties. The dilead(II) complexes were relatively insoluble and readily reformed from the transmetalation reaction mixture when attempts were made to isolate the transition metal complex. The use of either thiocyanate (in the case of the copper complexes) [11] or chloride (in the case of the cobalt complexes) [9,10] ions to precipitate the lead ions prior to isolation of the transition metal complex made it possible to isolate the desired complexes, albeit in relatively low yields. In order to try to (a) ease these synthetic

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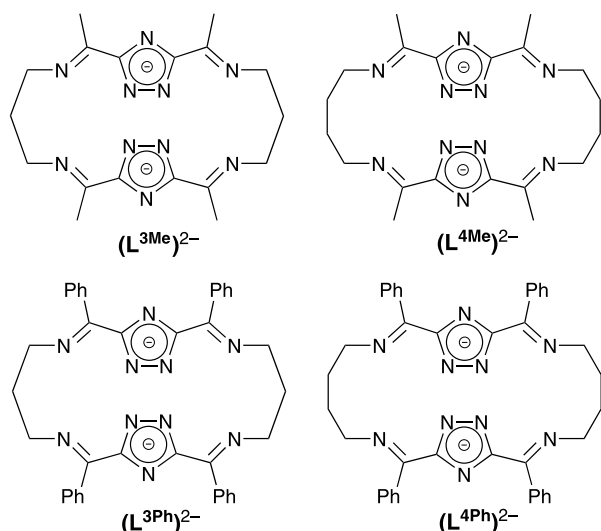
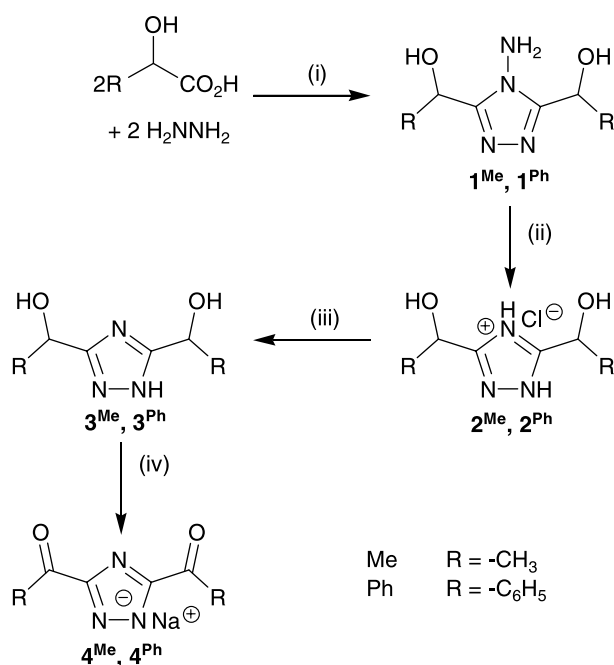


FIGURE 1 The known,  $(L^{3Me})^{2-}$  and  $(L^{4Me})^{2-}$ , and new,  $(L^{3Ph})^{2-}$  and  $(L^{4Ph})^{2-}$ , triazolate-containing Schiff-base macrocycles prepared by this research group.

challenges, (b) improve the solubility of the transition metal ion complexes in a wider range of organic solvents and (c) allow an investigation of the influence of the substituents on the electronic and magnetic properties of the resulting complexes, we developed the synthesis of a novel 3,5-diketo-1,2,4-triazolate, sodium 3,5-dibenzoyl-1,2,4-triazolate,  $4^{Ph}$  (Scheme 1). Here we report the synthesis of  $4^{Ph}$  and its use as a head unit in the Schiff-base macrocycles  $(L^{3Ph})^{2-}$  and  $(L^{4Ph})^{2-}$  (Fig. 1).



SCHEME 1 i) The *S*-enantiomer ( $1^{Me}$ ) or racemate ( $1^{Ph}$ ) of the appropriate  $\alpha$ -hydroxy acid was used as discussed in the text, 100–160°C, overnight; ii) HCl, NaNO<sub>2</sub>; iii) NaOH, CH<sub>3</sub>CN/H<sub>2</sub>O; iv) NaMnO<sub>4</sub>/H<sub>2</sub>O.

## RESULTS AND DISCUSSION

### Organic Synthesis

Torres and co-workers have reported the preparation of some 1,2,4-triazole-based dialcohols with  $C_2$ -symmetry [e.g.  $(S,S)$ - $1^{Me}$ ,  $(S,S)$ - $1^{Ph}$  and  $(S,S)$ - $1^{Bz}$ , Fig. 2] by the condensation of commercially available  $\alpha$ -hydroxy acids, such as lactic and phenyllactic acid, with hydrazine hydrate (Scheme 1, step i) [6,12]. Only one of these dialcohols,  $1^{Me}$  [4-amino-3,5-bis(1-hydroxyethyl)-1,2,4-triazole], was converted, using three more steps, into a 3,5-diketo-1,2,4-triazole (3,5-diacetyl-1*H*-1,2,4-triazole, the free acid of  $4^{Me}$ , Fig. 2, Scheme 1) in order to access Schiff-base macrocycles [6,13]. In our group, Torres' procedure for the synthesis of the free acid of  $4^{Me}$  has been modified slightly in order to provide a *sodium* 3,5-diketo-1,2,4-triazolate salt which is ready for direct use in template reactions. This modified protocol has also been applied to the preparation of another 3,5-diketo-1,2,4-triazolate, sodium 3,5-dibenzoyl-1,2,4-triazolate  $4^{Ph}$  (Scheme 1).

The  $C_2$ -symmetric dialcohol  $1^{Me}$  was synthesized and converted in two further steps into  $3^{Me}$  according to the procedures described by Torres and co-workers (Scheme 1) [6,12]. In the first step it was found to be necessary to use the pure *S*-enantiomer of lactic acid rather than the racemate, as the latter resulted in an oily mixture from which the desired product could not be separated. Oxidation of the two hydroxy groups in  $3^{Me}$  with sodium permanganate, in contrast to Torres *et al.* who used potassium permanganate, [13] yields the desired Schiff-base head unit as sodium 3,5-diacetyl-1,2,4-triazolate ( $4^{Me}$ ), initially in slightly impure form. The microanalyses of the crude powders obtained were consistent with them being  $4^{Me} \cdot NaOH \cdot 0.75(CH_3OH)$ . Recrystallization gave clean  $4^{Me}(H_2O)$  as confirmed by elemental analysis. The advantage of using sodium permanganate and thus producing the sodium triazolite salt lies in the following step, i.e. the lead templated Schiff-base cyclization reaction, and will be discussed later.

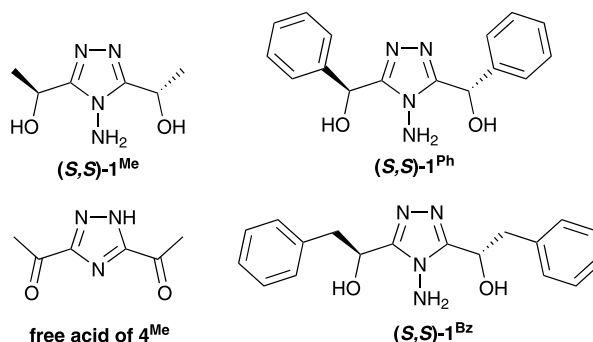


FIGURE 2 Some 3,5-disubstituted 1,2,4-triazoles described by Torres and co-workers.

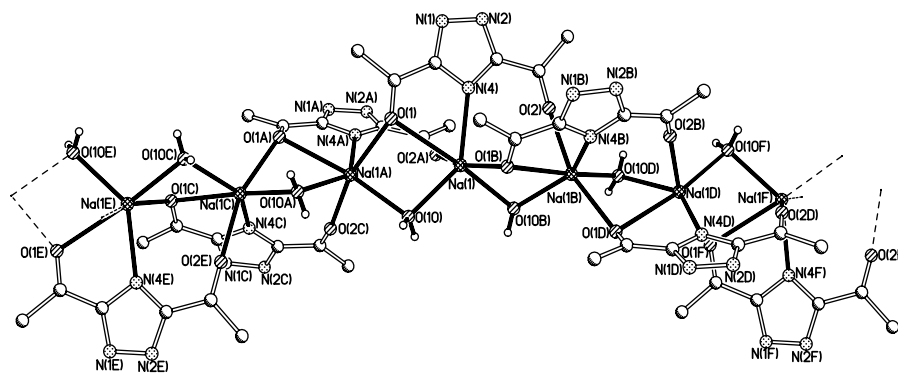


FIGURE 3 Perspective view of the polymer of sodium 3,5-diacetyl-1,2,4-triazolate monohydrate,  $[4^{\text{Me}}(\text{H}_2\text{O})]_{\infty}$ , showing the helical nature of the structure. Methyl hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: A =  $y, 1 - x + y, -\frac{1}{6} + z$ ; B =  $1 + x - y, +x, \frac{1}{6} + z$ ; C =  $1 - x + y, 2 - x, -\frac{1}{3} + z$ ; D =  $2 - y, 1 + x - y, \frac{1}{3} + z$ ; E =  $2 - x, 2 - y, -\frac{1}{2} + z$ ; F =  $2 - x, 2 - y, \frac{1}{2} + z$ .

4-Amino-3,5-bis-(1-hydroxy-1-phenylmethyl)-1,2,4-triazole ( $1^{\text{Ph}}$ ) was prepared as described by Torres and co-workers (Scheme 1, step i) [12]. In this case the use of the racemic mandelic acid, instead of the enantiomerically pure  $\alpha$ -hydroxy acid, caused no problems and  $1^{\text{Ph}}$  was obtained as a white powder in good yield. It was characterized by a comparison of the analytical data obtained with that given in the literature.

The same modified three step protocol for converting  $1^{\text{Me}}$  to  $4^{\text{Me}}$  was then successfully employed to convert  $1^{\text{Ph}}$  into  $4^{\text{Ph}}$  (Scheme 1). Deamination of  $1^{\text{Ph}}$  using  $\text{NaNO}_2/\text{HCl}$  gave 3,5-bis-(1-hydroxy-1-phenylmethyl)-1,2,4-triazole as the hydrochloride salt,  $2^{\text{Ph}}$ . The  $^1\text{H}$  NMR spectrum shows that the deamination was successful as the amino group signal at 5.83 ppm in  $1^{\text{Ph}}$  is absent from the spectrum of  $2^{\text{Ph}}$ . Neutralisation of  $2^{\text{Ph}}$  with aqueous  $\text{NaOH}$  gave 3,5-bis-(1-hydroxy-1-phenylmethyl)-1,2,4-triazole ( $3^{\text{Ph}}$ ) as a white powder in 97% yield. The composition of both  $2^{\text{Ph}}$  and  $3^{\text{Ph}}$  was confirmed by elemental analysis. The signals for the quaternary C(triazole), at 159.2 ppm ( $2^{\text{Ph}}$ ) and 162.3 ppm ( $3^{\text{Ph}}$ ) in the respective  $^{13}\text{C}$  NMR spectra, show that the triazole moiety is intact.

The isolation of the hydrochloride salt  $2^{\text{Ph}}$  is not necessary and both steps, the deamination and neutralization, can be performed in a one-pot

reaction. Analogously to the synthesis of  $1^{\text{Me}}$ , the final step, oxidation of the hydroxy groups in  $3^{\text{Ph}}$  to keto groups ( $4^{\text{Ph}}$ ), was carried out using sodium permanganate (Scheme 1, step iv). The oxidation gave 3,5-dibenzoyl-1,2,4-triazole as the sodium salt,  $4^{\text{Ph}}$ , initially in slightly impure form. The microanalyses of the crude powders obtained were consistent with them being  $4^{\text{Ph}}\cdot\text{NaOH}$ . Recrystallization gave clean  $[4^{\text{Ph}}(\text{CH}_3\text{OH})(\text{H}_2\text{O})]$  as confirmed by elemental analysis. The appearance of a band at  $1638\text{ cm}^{-1}$  in the IR spectrum and a signal at 186.5 ppm in the  $^{13}\text{C}$  NMR spectrum confirm the formation of the two carbonyl groups. The symmetrical patterns observed in the NMR spectra of  $4^{\text{Ph}}$  show that both alcohol groups have been oxidized.

### Crystal Structures of Solvates of $4^{\text{Me}}$ and $4^{\text{Ph}}$

Diketone  $4^{\text{Me}}$  crystallizes as the monohydrate from a *N,N*-dimethylformamide solution upon vapour diffusion of diethylether and the X-ray crystal structure has been determined (Fig. 3, Table I). The asymmetric unit comprises one sodium triazolate monohydrate moiety. The complex crystallized but was twinned via a two-fold rotation axis perpendicular to the the six-fold screw axis in the chiral space group  $P6_1$ . The Flack parameter refined to 0.1(5) so the presence of inversion twinning cannot be ruled out: if inversion

TABLE I Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for polymeric  $4^{\text{Me}}(\text{H}_2\text{O})$

Na(1)—O(2A)	2.300(2)	N(4)—Na(1)—O(1)	64.29(6)
Na(1)—O(1B)	2.3871(19)	O(10B)—Na(1)—O(1)	172.72(6)
Na(1)—N(4)	2.422(2)	Na(1)—O(10)	2.3772(17)
Na(1)...Na(1A)	3.6285(4)	Na(1)—O(10B)	2.4049(17)
		Na(1)—O(1)	2.770(2)
O(2A)—Na(1)—O(10)	92.37(7)	O(2A)—Na(1)—O(1A)	161.57(8)
O(10)—Na(1)—O(1B)	105.09(7)	O(2A)—Na(1)—O(10B)	90.48(7)
O(10)—Na(1)—O(10B)	102.89(5)	O(1B)—Na(1)—O(10B)	80.03(6)
O(2A)—Na(1)—N(4)	84.78(8)	O(10)—Na(1)—N(4)	137.35(7)
O(1B)—Na(1)—N(4)	86.26(7)	O(10B)—Na(1)—N(4)	119.65(7)
O(2A)—Na(1)—O(1)	83.70(7)	O(10)—Na(1)—O(1)	73.09(5)

Symmetry transformations used to generate equivalent atoms: A:  $y, -x + y + 1, z - 1/6$  B:  $x - y + 1, x, z + 1/6$ .

twinning is present then both right and left handed helices are present in the crystal but if inversion twinning is not present then there are crystals of the left handed helix and crystals of the right handed helix in the bulk sample. The sixfold screw axis leads to the  $4^{\text{Me}}(\text{H}_2\text{O})$  molecules forming a helical polymeric arrangement around the sodium backbone. The chain polymerization occurs via bridging oxygen atoms in the form of a water molecule, O(10), and one of the two carbonyl oxygen atoms, O(1). Overall each sodium atom is six coordinate, binding to the two of each of these types of bridging atoms as well as to the N(4) nitrogen of the triazole ring and a second, non-bridging, carbonyl oxygen atom from the next triazolate in the chain, O(2A). Hence the chain is held together not only by the two types of bridging oxygen atoms but also due to the fact that the non-bridging carbonyl oxygen atom of each triazolate binds to a sodium ion from the next portion of the chain. As might be anticipated, the bridging carbonyl oxygen atom makes the longest bond to sodium, 2.770(2) Å, with the remaining bond lengths ranging from 2.300(2) to 2.422(2) Å (Table I).

In principle, the anion required for charge balance against the sodium cation could have been either a deprotonated triazolate or the bridging water molecule instead being a bridging hydroxide ion. The two hydrogen atoms on O(10) were clearly observed in a difference map thus proving that this is indeed a water molecule rather than a hydroxide ion. Consistent with this, no significant electron density was observed near N(1) or N(2) indicating that neither nitrogen has a proton and hence that the positive charge from the sodium is balanced by the triazole having lost a proton to form a triazolate anion. The Na(1)—O—Na(1a) angles formed by the bridging oxygen atoms, O(1) and O(10), are 89.10(6)° and 98.71(6)° respectively.

The helical nature of the chain structure results in grooves into which neighbouring chains pack and this facilitates extensive intermolecular H-bonding between them. Specifically, the hydrogen atoms on the bridging water molecules, O(10), hydrogen bond to the triazolate nitrogen atoms, N(1) and N(2), of a neighbouring chain [N(1)'...O(10) 2.843 Å and N(2)'...O(10) 2.867 Å; N(1)'...H(10A)—O(10) 158.5° and N2'...H(10B)—O(10) 164.3°].

Recrystallization of  $4^{\text{Ph}}$ , the phenyl analogue of  $4^{\text{Me}}$ , from hot methanol gave good quality single crystals suitable for an X-ray structure determination (Fig. 4, Table II).

The phenyl groups present in  $4^{\text{Ph}}$  clearly have a dramatic impact on the nature of the structure formed as, in contrast to the polymeric structure of  $4^{\text{Me}}$  (in which methyl groups are present, Fig. 3), this complex crystallizes as a centrosymmetric dimer, featuring two  $\mu_2$ -bridging and two terminal methanol molecules (Fig. 4). Each sodium atom is six

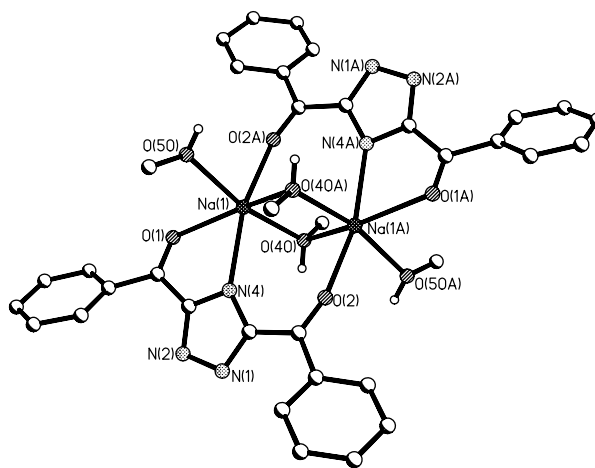


FIGURE 4 Perspective view of the dimer of sodium 3,5-dibenzoyl-1,2,4-triazolate,  $[4^{\text{Ph}}(\text{CH}_3\text{OH})_2]_2$ . Phenyl and methyl hydrogen atoms omitted for clarity. Symmetry transformation used to generate equivalent atoms:  $A = -x + 1, -y + 2, -z + 1$ .

coordinate comprising bonds from a carbonyl oxygen atom, O(1), and triazolate nitrogen atom, N(4), from one diketone, a carbonyl oxygen atom from the other diketone, O(2A), in addition to a terminal methanol and two bridging methanol molecules. Hence the dimer is held together not only by the two bridging methanol oxygen atoms but also by the dibenzoyl arms of the dibenzoyl-triazolate ligand spanning the two sodium ions. A narrower range of Na—X (X=N, O) bond lengths is observed in this structure [2.3149(9)–2.4739(9) Å, Table II], than was observed in the polymer of  $4^{\text{Me}}$  [2.300(2) to 2.422(2) plus 2.770(2) Å], presumably due to the reduced steric demand of forming a dimer rather than a polymeric chain. The Na(1)—O(40)—Na(1A) angle, 84.01(3)°, is more acute than those observed for the polymeric structure [89.10(6)° and 98.71(6)°] and correspondingly the distance between adjacent sodium atoms [3.2558 (8) Å] is shorter in this dimer than it was in the polymeric structure of  $4^{\text{Me}}$  [3.6285 (4) Å]. Once again the key hydrogen atoms, in this case on the methanol molecules, were located from difference maps, thus ruling out the possibility of there being methoxy rather than methanol groups present. This, combined with the lack of appropriate electron density near N(1) and N(2), clearly indicated that once again the charge balance for the positive sodium is a triazolate anion.

Intermolecular hydrogen bonding is present between the dimers. The methanol hydrogen atoms H(40) and H(50) are hydrogen bonded to nitrogen atoms N(1)' and N(2)', respectively, of the triazolate rings of neighbouring dimers [N(1)'...O(40) 2.826 Å and N2'...O(50) 2.827 Å; N(1)'...H(40)—O(40) 166.8° and N2'...H(50)—O(50) 167.8°]. Both of the phenyl rings are twisted well out of the plane of the triazolate ring (41.3° and 49.2°), and are at 20.9° to

TABLE II Bond lengths [Å] and angles [°] for  $[4^{\text{Ph}}(\text{CH}_3\text{OH})_2]_2$ .

Na(1)—O(2A)	2.3149(9)	O(2A)—Na(1)—O(50)	82.39(3)
Na(1)—O(50)	2.3404(9)	O(2A)—Na(1)—O(40)	82.74(3)
Na(1)—O(40)	2.3903(9)	O(50)—Na(1)—O(40)	164.88(3)
Na(1)—N(4)	2.4558(10)	O(2A)—Na(1)—N(4)	165.20(3)
Na(1)—O(1)	2.4709(9)	O(50)—Na(1)—N(4)	112.23(3)
Na(1)—O(40A)	2.4739(9)	O(40)—Na(1)—N(4)	82.74(3)
O(2)—Na(1A)	2.3148(9)	O(2A)—Na(1)—O(1)	117.47(3)
O(40)—Na(1A)	2.4739(9)	O(50)—Na(1)—O(1)	80.05(3)
Na(1)...Na(1A)	3.2558(8)	O(40)—Na(1)—O(1)	104.54(3)
N(4)—Na(1)—O(40A)	92.31(3)	N(4)—Na(1)—O(1)	69.26(3)
O(1)—Na(1)—O(40A)	149.96(3)	O(2A)—Na(1)—O(40A)	86.36(3)
	81.89(2)	O(50)—Na(1)—O(40A)	85.81(3)
	130.79(3)	O(40)—Na(1)—O(40A)	95.99(3)
	49.09(2)	Na(1)—O(40)—Na(1A)	84.01(3)
	86.44(3)		
	147.37(3)		
	46.90(2)		

Symmetry transformations used to generate equivalent atoms: A - x + 1, -y + 2, -z + 1.

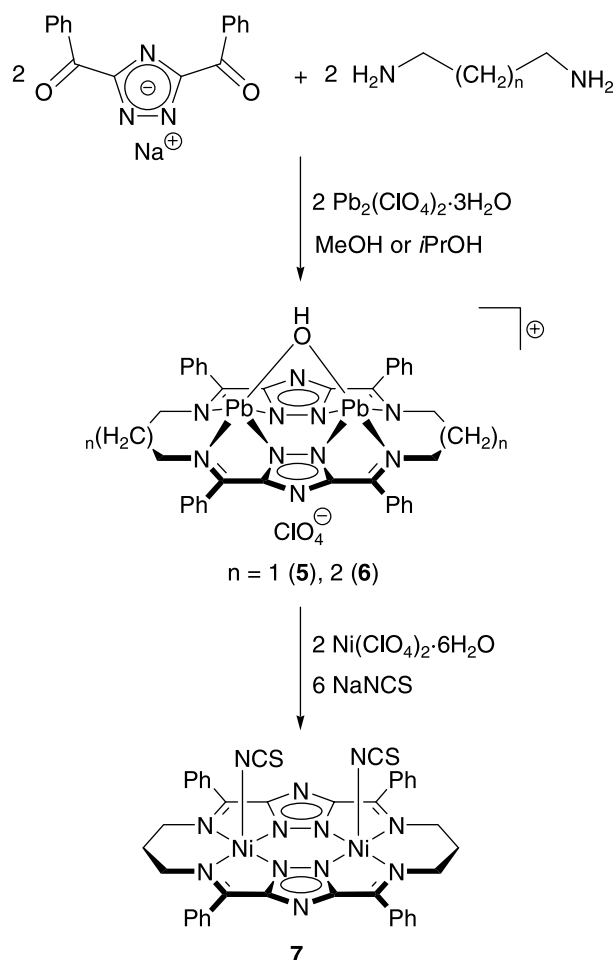
each other. The two carbonyl oxygen atoms, O(1) and O(2), are significantly out of the triazolate mean plane [by 0.532(2) and 0.376(2) Å respectively].

The sodium ions in  $[4^{\text{Me}}(\text{H}_2\text{O})]_{\infty}$  and  $[4^{\text{Ph}}(\text{CH}_3\text{OH})_2]_2$  are coordinated via  $N^4$  of the 1,2,4-triazolate ring, a relatively uncommon binding mode in our triazole research program. A search of the CSD (Version 5.27 Jan 2006) revealed no examples of sodium ions bound via  $N^4$  to triazole/triazolate-based ligands so these two complexes are the first of this type. In contrast, the CSD contains five structurally characterized examples of  $N^2$  coordination to sodium ions. Despite the fact that the triazole was bound through  $N^2$ , one of these structures, a network polymer by Orihuela *et al.*, [14] is topologically related to the structures described here because  $N^1$  is blocked as it forms part of a  $N^1,C^5$ -fused pyrimidine ring thus making  $N^2$  more like a lone nitrogen atom (and hence like  $N^4$ ) and, in addition, the  $N^1,C^5$ -fused pyrimidine ring has an oxygen substituent that makes a similar chelate ring on binding to the sodium ion as that made by the present ligands. In that structure the sodium ion was bridged to the next one in one direction by two water oxygen atoms and in the other direction by two oxygen donor atoms from two ligands. The  $\text{NO}_5$  coordination sphere of the sodium ion is not dissimilar to those found in the present structures, in particular to the  $\text{NO}_5$  coordination sphere of  $[4^{\text{Me}}(\text{H}_2\text{O})]_{\infty}$ .

### Macrocycle Synthesis

Utilizing our experience in the synthesis of the analogous diacetyltriazolate-containing macrocycles ( $\text{L}^{3\text{Me}}\text{2}^-$  and  $\text{L}^{4\text{Me}}\text{2}^-$ , [9–11] the Schiff-base macrocycles ( $\text{L}^{3\text{Ph}}\text{2}^-$  and  $\text{L}^{4\text{Ph}}\text{2}^-$  were formed by the addition of  $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$  to a solution of sodium 3,5-dibenzoyl-1,2,4-triazolate ( $4^{\text{Ph}}$ ) in methanol or *iso*-propanol, respectively, followed by heating to

reflux and the dropwise addition of 1,3-diaminopropane or 1,4-diaminobutane, respectively (Scheme 2). The resulting precipitate was filtered off giving the pure lead(II) complexes  $[\text{Pb}_2\text{L}^{3\text{Ph}}(\mu\text{-OH})]\text{ClO}_4$  (5) and  $[\text{Pb}_2\text{L}^{4\text{Ph}}(\mu\text{-OH})]\text{ClO}_4$  (6), in 82% and 54% yield, respectively. The use of the sodium salt of the triazolite head unit is the key to this step, since the



SCHEME 2 Synthesis of the new Schiff base macrocyclic complexes 5–7.

use of the potassium salt would also lead to the precipitation of  $\text{KClO}_4$  and thus prevent the precipitation of pure lead-templated macrocyclic complex. i.e.  $\text{NaClO}_4$  is far more soluble than  $\text{KClO}_4$  in the solvents used and it stays in solution. The presence of a  $\mu$ -hydroxo group is not found for the analogous dilead(II) complexes of the macrocycles ( $\text{L}^{3\text{Me}}\text{)}^{2-}$  and ( $\text{L}^{4\text{Me}}\text{)}^{2-}$ , [9–11] although it has been observed in a dimeric dilead(II) complex of a related pyridazine-based Schiff-base macrocycle [15]. It was initially thought that the presence of the  $\mu$ -hydroxo group was due to the use of the crude head unit, which appeared to be a 1:1 adduct of sodium 1,2,4-triazolate  $\mathbf{4}^{\text{Ph}}$  and sodium hydroxide,  $\mathbf{4}^{\text{Ph}}\cdot\text{NaOH}$ , as the starting material. However when the crude head unit was recrystallized and the reaction repeated with clean  $\mathbf{4}^{\text{Ph}}$ , microanalysis and IR data on the product complex indicated that the  $\mu$ -hydroxo group was still present. The lower yield for **6** is thought to be caused by the higher solubility of the butylene derivative, perhaps combined with the effects of a poorer fit of the lead(II) ions to the larger macrocyclic cavity. The bands observed at  $1615\text{ cm}^{-1}$  (**5**) and  $1616\text{ cm}^{-1}$  (**6**) in the IR spectra of the two complexes confirm the formation of the imine bonds. The NMR spectra show that both dilead(II) complexes are symmetrical in solution. This leads to the proposed structures (Scheme 2) in which the metal centres are bridged by a hydroxide ion. Whether the complexes are monomeric or dimeric cannot be decided without an X-ray crystal structure determination. The dimerization of dilead(II)-hydroxo-complexes in the solid state has been observed for a similar, pyridazine-containing, [2 + 2] Schiff-base macrocycle [15]. The bands for the perchlorate ion, in the IR spectra of **5** and **6**, are split, indicating that there may be an interaction of the perchlorate ion with at least one metal centre in the solid state. The presence of a hydroxo group in these two dilead(II)-complexes is a feature of the new macrocycles ( $\text{L}^{3\text{Ph}}\text{)}^{2-}$  and ( $\text{L}^{4\text{Ph}}\text{)}^{2-}$ .

An attempt to prepare a dinickel(II)-complex of ( $\text{L}^{3\text{Ph}}\text{)}^{2-}$  was made by transmetalation of **5** in  $\text{CH}_3\text{CN}$  with two equivalents of  $\text{Ni}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ . Normally, the resulting transmetalation solution would simply have been concentrated, resulting in either precipitation of the desired complex or in a solution which on vapour diffusion of  $\text{Et}_2\text{O}$  would yield the desired complex. However, in this case vapour diffusion of  $\text{Et}_2\text{O}$  into the concentrated green reaction solution caused the colour to fade and, along with a green crystalline product, a white, presumably lead-containing precipitate formed. Attempts to separate these two products proved to be unsuccessful. A similar problem had been observed for the transmetalation of the dilead ( $\text{L}^{3\text{Me}}\text{)}^{2-}$  and ( $\text{L}^{4\text{Me}}\text{)}^{2-}$  macrocyclic complexes with Co(II)- [9,10] and Cu(II)-salts [11]. As discussed in the Cu(II) paper, the addition of four equivalents of

$\text{NaNCS}$  per dilead macrocycle led to the precipitation of  $\text{Pb}(\text{NCS})_2$ , which was easily removed by filtration, allowing the copper complex to then be isolated cleanly. However, in the case of ( $\text{L}^{3\text{Ph}}\text{)}^{2-}$ , no pure  $[\text{Ni}_2\text{L}^{3\text{Ph}}(\text{CH}_3\text{CN})_4](\text{ClO}_4)_2$  could be obtained by this method.

The treatment of the reaction mixture with two additional equivalents of  $\text{NaNCS}$  leads to the successful formation of  $[\text{Ni}_2\text{L}^{3\text{Ph}}(\text{NCS})_2]$  (**7**), which can be isolated in microanalytically pure form as green crystals in 25% yield (Scheme 2). A band at  $1603\text{ cm}^{-1}$  in the IR spectrum of **7** shows that the imine bonds remain intact. The presence of two bands due to the thiocyanate CN stretches, at  $2102$  and  $2089\text{ cm}^{-1}$ , indicates that the two thiocyanate ions are in slightly different environments. Unambiguous assignment of these bands is not possible considering the overlapping ranges of wavenumbers observed for the wide variety of possible coordination modes of thiocyanate, [16] however, the X-ray structure determination reveals that both are N-bound (Fig. 5).

Green single crystals of **7**·0.5MeCN were obtained by vapour diffusion of  $\text{Et}_2\text{O}$  into the reaction solution and the X-ray crystal structure determined (Fig. 5, Table III). This revealed that the complex contains two, crystallographically independent, distorted square pyramidal Ni(II) centres which are doubly bridged by the triazolate moieties provided by the ( $\text{L}^{3\text{Ph}}\text{)}^{2-}$  macrocyclic framework (Fig. 5). The macrocycle provides four equatorial donor atoms, two imine and two triazolate nitrogen

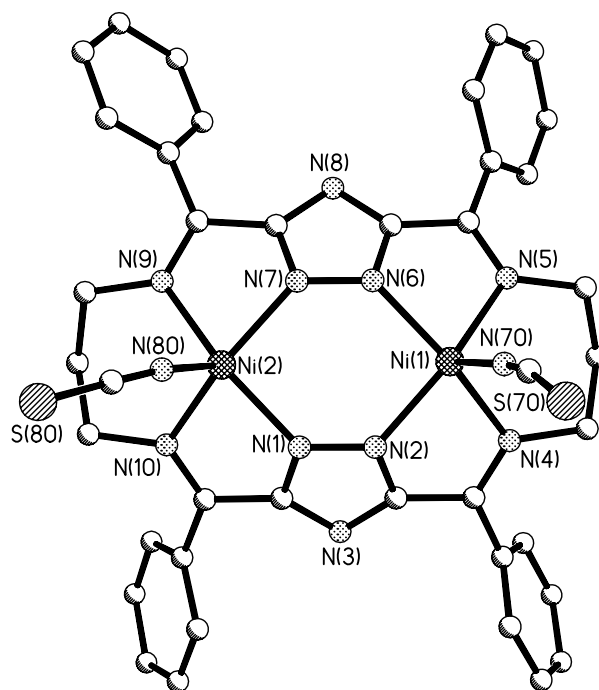


FIGURE 5 Perspective view of **7**. Hydrogen atoms and the lower occupancy component of the disordered thiocyanate omitted for clarity.

TABLE III Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for 7·0·5MeCN.

Ni(2)–N(80)	1.957(2)	N(80)–Ni(2)–N(9)	97.38(8)
Ni(2)–N(7)	2.0107(17)	N(7)–Ni(2)–N(9)	79.20(7)
Ni(2)–N(1)	2.0206(16)	N(1)–Ni(2)–N(9)	152.75(7)
Ni(2)–N(10)	2.0412(18)	N(10)–Ni(2)–N(9)	93.13(7)
Ni(2)–N(9)	2.0651(18)	N(70)–Ni(1)–N(6)	107.94(8)
Ni(1)–N(70)	1.966(2)	N(70)–Ni(1)–N(2)	106.20(8)
Ni(1)–N(6)	1.9984(17)	N(6)–Ni(1)–N(2)	95.30(7)
Ni(1)–N(2)	2.0217(17)	N(70)–Ni(1)–N(4)	99.04(8)
Ni(1)–N(4)	2.0377(17)	N(6)–Ni(1)–N(4)	152.83(7)
Ni(1)–N(5)	2.0496(17)	N(2)–Ni(1)–N(4)	79.87(7)
Ni(1)···Ni(2)	4.0616 (4)	N(70)–Ni(1)–N(5)	99.80(8)
N(80)–Ni(2)–N(7)	110.12(8)	N(6)–Ni(1)–N(5)	79.70(7)
N(80)–Ni(2)–N(1)	109.56(8)	N(2)–Ni(1)–N(5)	153.78(7)
N(7)–Ni(2)–N(1)	94.86(7)	N(4)–Ni(1)–N(5)	92.84(7)
N(80)–Ni(2)–N(10)	98.57(8)	C(70)–N(70)–Ni(1)	170.8(2)
N(7)–Ni(2)–N(10)	150.97(7)	N(70)–C(70)–S(70)	168.4(3)
N(1)–Ni(2)–N(10)	79.17(7)	N(70)–C(70)–S(71)	166.6(3)
		C(80)–N(80)–Ni(2)	163.4(2)
		N(80)–C(80)–S(80)	178.8(2)

atoms, to each Ni(II) ion. In each case the fifth, axial, coordination site is occupied by an N-bound thiocyanate ion. Both nickel ions are considerably raised out of the mean plane of the four equatorial nitrogen donor atoms towards the axially coordinated thiocyanate ion [Ni(1) 0.4673(9)  $\text{\AA}$ ; Ni(2) 0.4942(9)  $\text{\AA}$ ]. The Ni–N<sub>triazolate</sub> bond lengths are slightly shorter than the Ni–N<sub>imine</sub> bond lengths (Ni–N<sub>triazolate</sub> average 2.013  $\text{\AA}$ , Ni–N<sub>imine</sub> average 2.048  $\text{\AA}$ , Table III), as seen in related triazolate macrocyclic structures [9,10,11]. The bonds to the axially bound thiocyanate nitrogen atom [Ni(1) 1.966(2)  $\text{\AA}$ ; Ni(2) 1.957(2)  $\text{\AA}$ ] are significantly shorter than either of these two sets of Ni–N<sub>equatorial</sub> bond lengths. As expected, the N<sub>triazolate</sub>–Ni–N<sub>imine</sub> bond angles are quite small [79.17(7)–79.87(7) $^\circ$ ] while the N<sub>imine</sub>–Ni–N<sub>imine</sub> [92.84(7)–93.13(7) $^\circ$ ] and N<sub>triazolate</sub>–Ni–N<sub>triazolate</sub> [94.86(7)–95.30(7) $^\circ$ ] bond angles are larger. The relatively unconstrained N<sub>imine</sub>–Ni–N<sub>NCS</sub> and N<sub>triazolate</sub>–Ni–N<sub>NCS</sub> bond angles fall in the ranges 97.38(8)–99.8(8) $^\circ$  and 106.20(8)–110.12(8) $^\circ$ , respectively.

The distorted square pyramidal Ni(II) coordination sphere in 7·0·5MeCN is similar to that observed in a high spin mononuclear complex, [Ni(N<sub>3</sub>As)(NCS)<sub>2</sub>], reported by Sacconi *et al.* [17,18]. The Ni(II) ion in [Ni(N<sub>3</sub>As)(NCS)<sub>2</sub>] is raised out of the N<sub>4</sub> equatorial coordination plane (3 N from the N<sub>3</sub>As ligand and 1 N from an N-bound thiocyanate) towards the axial thiocyanate ion by 0.34  $\text{\AA}$ , slightly less than the values observed for the two Ni(II) centres in 7·0·5MeCN. The Ni–N<sub>equatorial</sub> bond lengths in [Ni(N<sub>3</sub>As)(NCS)<sub>2</sub>] span quite a large range, 1.96(1)  $\text{\AA}$  to 2.22(1)  $\text{\AA}$  (the shortest involves the equatorially bound thiocyanate). The Ni–N<sub>equatorial</sub> bond lengths in 7·0·5MeCN lie within that range, but are less widely varied [1.9984(17)–2.0651(18)  $\text{\AA}$ ]. As is observed in 7·0·5MeCN, the Ni–NCS(axial) bond length in [Ni(N<sub>3</sub>As)(NCS)<sub>2</sub>], 1.95(1)  $\text{\AA}$ , is shorter than any of the Ni–N<sub>equatorial</sub> bond lengths. The range of

cis–N<sub>equatorial</sub>–Ni–N<sub>equatorial</sub> bond angles in [Ni(N<sub>3</sub>As)(NCS)<sub>2</sub>], 82.5(4)–94.4(4) $^\circ$ , is similar to the range seen in 7·0·5MeCN, 79.17(7)–95.30(7) $^\circ$ . In the case of the N<sub>equatorial</sub>–Ni–N<sub>axial</sub> bond angles, somewhat more obtuse angles are observed for 7·0·5MeCN [99.04(8)–109.56(8) $^\circ$ ] than for [Ni(N<sub>3</sub>As)(NCS)<sub>2</sub>] [98.5(4)–100.4(5) $^\circ$ ], as in the former complex the Ni(II) centres are somewhat further out of the N<sub>4</sub> basal plane. The nickel(II) ion in [Ni(N<sub>3</sub>As)(NCS)<sub>2</sub>] was established to be high spin ( $\mu_{\text{eff}} = 3.37$  B.M.) [18] and it appears that the nickel(II) ions in 7·0·5MeCN are likewise high spin ( $\mu_{\text{eff}}$  ca. 3.28 per Ni).

The macrocycle conformation in 7·0·5MeCN is far from flat. The mean planes of the two triazolate rings intersect at 77.91(7) $^\circ$ , an almost right angular fold, and in the other direction the mean planes of the two sets of equatorial N<sub>4</sub> donors atoms intersect at an angle of 38.97(6) $^\circ$ . It is clear that, despite the potential for conjugation throughout the phenyl, imine and triazolate moieties, these three moieties are far from perfectly co-planar. For example, the phenyl ring mean planes are twisted out of the plane of the attached triazolate moiety mean plane by angles ranging from 40.02(8) $^\circ$  to 85.22(7) $^\circ$  and the imine nitrogen atoms are also twisted well out of the associated triazolate mean plane [from 0.6001(41)  $\text{\AA}$  for N(5) to 0.7546(39)  $\text{\AA}$  for N(4)].

The overall structure of this Ni(II) complex of the (L<sup>3Ph</sup>)<sup>2-</sup> macrocycle is not dissimilar to that of the five-coordinate complexes, [Cu<sub>2</sub>L<sup>3Me</sup>(NCS)<sub>2</sub>] and [Co<sub>2</sub>L<sup>3Me</sup>Cl<sub>2</sub>], reported earlier by this group [(L<sup>3Me</sup>)<sub>2</sub><sup>2-</sup>, Fig. 1] [10, 11]. There the metal centres were separated by 4.075(3) and 4.280(1)  $\text{\AA}$ , respectively, and the triazolate rings were angled at 69.1(2) and 85.52(8) $^\circ$ , respectively, both of which are similar to the Ni···Ni separation and triazolate fold observed in 7·0·5MeCN. The metal ions in those two structures were pulled out of the N<sub>4</sub> equatorial plane towards the axial substituent [by 0.477(3)–0.485(3) and 0.835(1)  $\text{\AA}$ , respectively] as seen in 7·0·5MeCN. The



phenyl rings seem to have had little effect on the overall structure when compared to these methyl substituted analogues: the differences that are observed are likely due to the presence of a different metal ion. There are only two structurally characterized examples of dinickel complexes of acyclic 3,5-disubstituted 1,2,4-triazoles and both contain two octahedral nickel(II) ions doubly bridged by triazole moieties [19]. The complex 7·0.5MeCN is the first example of a structurally characterised nickel complex of any triazolate macrocycle.

## CONCLUSION

Based on the synthesis of (*RS*)-4-amino-3,5-bis-(1-hydroxy-1-phenylmethyl)-1,2,4-triazole (**1<sup>Ph</sup>**) [12] and 3,5-diacetyl-1,2,4-triazole [13] we have developed an optimised synthesis of sodium 3,5-diacetyl-1,2,4-triazolate (**4<sup>Me</sup>**) and the new phenyl-substituted triazole head unit sodium 3,5-dibenzoyl-1,2,4-triazolate (**4<sup>Ph</sup>**). That **4<sup>Ph</sup>** can be used in the synthesis of Schiff-base macrocycles has been demonstrated by the formation of [Pb<sub>2</sub>L<sup>3Ph</sup>(μ-OH)]ClO<sub>4</sub> (**5**) and [Pb<sub>2</sub>L<sup>4Ph</sup>(μ-OH)]ClO<sub>4</sub> (**6**). Although the difficulties encountered in the transmetallation reactions of the **4<sup>Me</sup>** derived acetyl-analogues were not avoided by use of these new, *much more soluble*, phenyl-analogues, we were able to isolate and crystallographically characterize a new, nicely soluble, dinickel(II)-complex. It is notable that 7·0.5MeCN is the first example of a structurally characterized nickel complex of any triazolate macrocycle. Further modifications to the macrocycle framework by the development of other new triazole-based building blocks are clearly necessary and work in these directions is well underway [20].

## EXPERIMENTAL

All reagents and solvents were used as received, without further purification, unless otherwise stated. 4-Amino-3,5-bis-(1-hydroxyethyl)-1,2,4-triazole (**1<sup>Me</sup>**) and 4-amino-3,5-bis-(1-hydroxy-1-phenylmethyl)-1,2,4-triazole (**1<sup>Ph</sup>**) were synthesized as reported in the literature using the *S*-enantiomer of lactic acid and racemic mandelic acid respectively [12]. The two step conversion of **1<sup>Me</sup>** into **3<sup>Me</sup>** was carried out according to the literature [13]. Acetonitrile was refluxed over calcium hydride and distilled prior to use. Measurements were carried out as described previously [4,21].

**Extreme CAUTION!** Whilst no problems were encountered in the course of this work, perchlorate salts, hydrazine and hydrazides are potentially

explosive and should therefore be handled with appropriate care.

### Sodium 3,5-diacetyl-1,2,4-triazolate (**4<sup>Me</sup>**)

**3<sup>Me</sup>** (2.4 g, 15.5 mmol) is added to water (50 ml) and heated to 80°C. A hot solution of sodium permanganate monohydrate (5.3 g, 33 mmol) in water (200 ml) is added dropwise. The reaction mixture is stirred at 80°C for two hours. The suspension is filtered whilst still hot and thoroughly washed with hot water. After removing the aqueous solvents the solid residue is dried under vacuum and then extracted with 100 ml MeOH at room temperature. Filtration of the undissolved residue and evaporation of the solvent yield a pale-yellowish solid which is dried under reduced pressure to give a crude white powder with a microanalysis which is consistent with sodium 3,5-diacetyl-1,2,4-triazolate·NaOH·0.75(CH<sub>3</sub>OH) (2.1 g, 73%). Anal. found C, 34.44; H, 3.84; N, 18.43; C<sub>6</sub>H<sub>6</sub>N<sub>3</sub>O<sub>2</sub>·Na·NaOH·0.75(CH<sub>3</sub>OH) requires C, 33.90; H, 4.21; N, 17.57%. MS (ESI neg.) (*m/z*): 152. <sup>1</sup>H NMR (D<sub>2</sub>O): 2.67 (singlet, CH<sub>3</sub>). Recrystallization of the crude white solid (0.100 g) from ca. 2 mL DMF by vapour diffusion of diethyl ether gives colourless, twinned, crystals of sodium 3,5-diacetyl-1,2,4-triazolate monohydrate [**4<sup>Me</sup>**(H<sub>2</sub>O)]<sub>∞</sub> (70 mg, 88%). Anal. found C, 37.31; H, 4.46; N, 21.60; C<sub>6</sub>H<sub>6</sub>N<sub>3</sub>O<sub>2</sub>·Na·H<sub>2</sub>O requires C, 37.31; H, 4.18; N, 21.76%.

### 3,5-Bis-(1-hydroxy-1-phenylmethyl)-1,2,4-triazole Hydrochloride (**2<sup>Ph</sup>**)

4-Amino-3,5-bis-(1-hydroxy-1-phenyl-methyl)-1,2,4-triazole (**1<sup>Ph</sup>**, 11.4 g, 38.5 mmol) is dissolved in 180 ml 6N HCl. The mixture is cooled down to 0°C and a prechilled solution of 7.50 g (96.2 mmol) NaNO<sub>2</sub> in 65 ml H<sub>2</sub>O and 25 g ice is added via a dropping funnel at such rate so as to maintain the temperature strictly below 5°C. After the addition is complete, the mixture is stirred at 5°C for two hours and then overnight at room temperature. All volatile ingredients are removed *in vacuo* and the residue is extracted with hot CH<sub>3</sub>CN (3 × 400 ml). The clear filtrate is evaporated to dryness to obtain the product as a white powder which is dried *in vacuo* (5.05 g, 41%). Anal. found C, 60.07; H, 5.27; N, 13.23; Cl, 11.20%. C<sub>16</sub>H<sub>16</sub>ClN<sub>3</sub>O<sub>2</sub> requires: C, 60.47; H, 5.08; N, 13.22; Cl, 11.16%. IR (KBr):  $\nu = 3351, 3045, 2893, 2641, 1691, 1596, 1497, 1451, 1409, 1321, 1234, 1177, 1059, 1001, 887, 838, 727, 697, 624, 544, 491, 472 \text{ cm}^{-1}$ . NMR(DMSO-*d*<sub>6</sub>):  $\delta_{\text{H}}$  (500 MHz) 5.99 (d, <sup>3</sup>*J* = 5.0 Hz, 2H, CH), 7.28–7.49 (m, 10H, H<sub>phenyl</sub>), the signals of OH- and NH-groups could not be detected;  $\delta_{\text{C}}$  (125 MHz) 67.3 (s, CH), 126.6, 128.1, 128.4, 140.3 (s, *ipso*-C), 159.2 (s, C<sub>triazole</sub>).

### 3,5-Bis-(1-hydroxy-1-phenylmethyl)-1,2,4-triazole ( $3^{\text{Ph}}$ )

A solution of 5.00 g (15.7 mmol) of 3,5-bis-(1-hydroxy-1-phenylmethyl)-1,2,4-triazole hydrochloride ( $2^{\text{Ph}}$ ) in 300 ml  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (1:1) is neutralized with aqueous NaOH (40%) and the mixture stirred for one hour to give a pale yellow solution. Removing of all volatiles leaves a white precipitate, which is extracted with  $\text{CH}_3\text{CN}$  ( $5 \times 200$  ml). Evaporation of the solvent *in vacuo* yields the product as a white powder (4.28 g, 97%). Anal. found C, 66.68; H, 5.28; N, 14.80%;  $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_2 \cdot 1/3\text{H}_2\text{O}$  requires: C, 66.89; H, 5.50; N, 14.62%. IR (KBr):  $\nu = 3160, 2908, 1619, 1493, 1455, 1401, 1348, 1260, 1192, 1135, 1036, 1017, 918, 864, 811, 746, 697, 620, 525, 480 \text{ cm}^{-1}$ . NMR ( $\text{DMSO}-d_6$ ):  $\delta_{\text{H}}$  (500 MHz) 5.76 (s, 2H, CH), 7.20–7.45 (m, 10H,  $\text{H}_{\text{Phenyl}}$ ), the signals of OH and NH-groups could not be detected;  $\delta_{\text{C}}$  (125 MHz) 69.0 (s, CH), 126.6, 127.1, 128.0, 143.0 (s, *ipso-C*), 162.3 (s,  $\text{C}_{\text{triazole}}$ ).

### Sodium 3,5-dibenzoyl-1,2,4-triazolate ( $4^{\text{Ph}}$ )

A solution of 5.20 g (32.4 mmol)  $\text{NaMnO}_4 \cdot \text{H}_2\text{O}$  in 200 ml  $\text{H}_2\text{O}$  is added dropwise to a heated suspension of 4.28 g (15.2 mmol) 3,5-bis-(1-hydroxy-1-phenylmethyl)-1,2,4-triazole ( $3^{\text{Ph}}$ ) in 150 ml  $\text{H}_2\text{O}$  *via* a dropping funnel. After complete addition, the reaction mixture is stirred at  $80^\circ\text{C}$  for 2 hours after which it is filtered through a Büchner funnel whilst still hot and thoroughly washed with hot water. After removing the aqueous solvent *in vacuo*, the solid residue is extracted with 250 ml MeOH. Filtration and evaporation of the solvent yielded a crude white powder with a microanalysis which is consistent with  $4^{\text{Ph}} \cdot \text{NaOH}$  (3.17 g, 62%). Anal. found C, 56.67; H, 3.77; N, 12.05;  $\text{C}_{16}\text{H}_{11}\text{N}_3\text{Na}_2\text{O}_3$  requires C, 56.64; H, 3.27; N, 12.39. IR (KBr):  $\nu = 2908, 1638 (\text{C}=\text{O}), 1447, 1390, 1314, 1238, 1226, 1177, 1112, 1028, 937, 925, 750, 693, 678, 655 \text{ cm}^{-1}$ . NMR ( $\text{D}_6\text{-DMSO}$ ):  $\delta_{\text{H}}$  (500 MHz) 7.54 (td,  $^2J = 6.8 \text{ Hz}$ ,  $^3J = 1.5 \text{ Hz}$ , 4H, *ortho-H*), 7.62 (tt,  $^2J = 7.5 \text{ Hz}$ ,  $^3J = 1.5 \text{ Hz}$ , 2H, *para-H*), 8.41 (dt,  $^2J = 7.5 \text{ Hz}$ ,  $^2J = 6.8 \text{ Hz}$ , 4H, *meta-H*);  $\delta_{\text{C}}$  (125 MHz) 128.0, 130.6, 132.2, 138.3 (s, *ipso-C*), 162.4 (s,  $\text{C}_{\text{triazole}}$ ), 186.5 (s,  $\text{C}=\text{O}$ ). Recrystallization of the crude white solid from hot methanol gives colourless single crystals of  $[4^{\text{Ph}}(\text{CH}_3\text{OH})_2]_2$ . Repeating this in bulk, 0.321 g (0.947 mmol) of the white powder was dissolved in ca. 17 mL of boiling methanol and left to cool to room temperature, resulting in the formation of colourless crystals. A second crop was obtained from the filtrate on cooling in a freezer and a third on concentrating the filtrate to ca. 2 mL and again cooling in a freezer. The crystals were combined, washed with ice-cold methanol and dried (0.273 g, 82%). Anal. found C, 58.37; H, 4.58; N, 11.94%;

$\text{C}_{16}\text{H}_{10}\text{N}_3\text{O}_2\text{Na} \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$  [ $4^{\text{Ph}}(\text{CH}_3\text{OH})(\text{H}_2\text{O})$ ] requires C, 58.45; H, 4.62; N, 12.03%.

### $\text{Pb}_2\text{L}^{3\text{Ph}}(\mu\text{-OH})\text{ClO}_4$ (5)

$\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$  (590 mg, 1.45 mmol) in 10 ml MeOH is added dropwise to a heated solution of 513 mg (1.45 mmol) sodium 3,5-dibenzoyl-1,2,4-triazolate ( $4^{\text{Ph}}$ ) in 40 ml MeOH. During the addition the solution becomes cloudy first and then clears again. Then, 108 mg (1.45 mmol) 1,3-diaminopropane in 10 ml MeOH are added dropwise, and a white precipitate forms. After refluxing overnight, the cold mixture is filtered. Washing of the white precipitate with cold MeOH and drying gives  $[\text{Pb}_2\text{L}^{3\text{Ph}}(\mu\text{-OH})\text{ClO}_4]$  (5) (686 mg, 82%). Anal. found C, 39.02; H, 2.66; N, 12.00; Cl, 3.03%;  $\text{C}_{38}\text{H}_{33}\text{ClN}_{10}\text{O}_5\text{Pb}_2$  requires C, 39.36; H, 2.87; N, 12.08; Cl 3.06%. IR (KBr):  $\nu = 3198 (\text{OH}), 3053 (\text{CH}_{\text{arom.}}), 2923 (\text{CH}_2), 1615 (\text{C}=\text{N}), 1573, 1466, 1440, 1409, 1352, 1321, 1238, 1108 + 1089 [\mu(\text{ClO}_4^-)], 1055, 956, 910, 777, 754, 704, 697 [\delta(\text{ClO}_4^-)], 620$ . NMR ( $\text{DMF}-d_7$ ):  $\delta_{\text{H}}$  (500 MHz) 1.85 [br,  $\mu\text{-OH}$ ], 3.60 (m, 4H,  $\text{CH}_2\text{CH}_2\text{N}$ ), 3.81 (m, 8H,  $\text{CH}_2\text{CH}_2\text{N}$ ), 7.37–7.51 (m, 20H,  $\text{H}_{\text{Ph}}$ );  $\delta_{\text{C}}$  (125 MHz) 32.3 (s,  $\text{CH}_2\text{CH}_2\text{N}$ ), 54.0 (s,  $\text{CH}_2\text{CH}_2\text{N}$ ), 128.8, 129.2, 130.3 (each s, *ortho*-, *meta*- and *para*-C), 133.3 (s, *ipso*-C), 160.7, 169.8 (each s,  $\text{C}=\text{N}$  and  $\text{C}_{\text{triazole}}$ ).

### $\text{Pb}_2\text{L}^{4\text{Ph}}(\mu\text{-OH})\text{ClO}_4$ (6)

$\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$  (366.9 mg, 0.90 mmol) in 10 ml  $^i\text{PrOH}$  is added dropwise to a heated solution of 320 mg (0.90 mmol) sodium 3,5-dibenzoyl-1,2,4-triazolate ( $4^{\text{Ph}}$ ) in 50 ml  $^i\text{PrOH}$ . During the addition the solution becomes cloudy first and then it clears again. Then, 79.4 mg (0.90 mmol) 1,4-diaminobutane in 10 ml  $^i\text{PrOH}$  are added dropwise, and a white precipitate forms. After refluxing overnight, the cold mixture is filtered. Washing of the white precipitate with cold  $^i\text{PrOH}$  and drying gives a white powder, which is extracted with 250 ml  $\text{CH}_3\text{CN}$ . Evaporation of the extract gives  $[\text{Pb}_2\text{L}^{4\text{Ph}}(\mu\text{-OH})\text{ClO}_4]$  (6) as a white solid, which is dried *in vacuo* (287.8 mg, 54%). Anal. found C, 39.90; H, 2.92; N, 11.30; Cl 3.09%;  $\text{C}_{40}\text{H}_{37}\text{ClN}_{10}\text{O}_5\text{Pb}_2$  requires C, 40.45; H, 3.14; N, 11.79; Cl 2.99%. IR (KBr):  $\nu = 3213 (\text{OH}), 3053 (\text{CH}_{\text{arom.}}), 2927, 2847 (\text{CH}_2), 1616 (\text{C}=\text{N}), 1596, 1575, 1492, 1464, 1447, 1409, 1352, 1319, 1232, 1178, 1116 + 1087 [\mu(\text{ClO}_4^-)], 1011, 847, 782, 744, 707 + 696 [\delta(\text{ClO}_4^-)], 657, 624$ ; NMR ( $\text{DMF}-d_7$ ):  $\delta_{\text{H}}$  (500 MHz) 1.86 [s(br),  $\mu\text{-OH}$ ], 3.49 [m(br), 8H,  $\text{CH}_2\text{CH}_2\text{N}$ ], 3.76 (m, 8H,  $\text{CH}_2\text{CH}_2\text{N}$ ), 7.26–7.62 (m, 20H,  $\text{H}_{\text{Ph}}$ );  $\delta_{\text{C}}$  (125 MHz) 28.8 (s,  $\text{CH}_2\text{CH}_2\text{N}$ ), 54.5 (s,  $\text{CH}_2\text{CH}_2\text{N}$ ), 130.0, 131.4, 134.3 (each s, *ortho*-, *meta*- and *para*-C), 136.9 (s, *ipso*-C), 164.5, 167.1 (each s,  $\text{C}=\text{N}$  and  $\text{C}_{\text{triazole}}$ ).

### Ni<sub>2</sub>L<sup>3Ph</sup>(NCS)<sub>2</sub> (7)

A solution of 66.4 mg (0.18 mmol) Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in 10 ml CH<sub>3</sub>CN is added dropwise to a heated solution of 105.3 mg (90.8 μmol) [Pb<sub>2</sub>L<sup>3Ph</sup>(μ-OH)]ClO<sub>4</sub> (5) 25 ml CH<sub>3</sub>CN. The mixture is refluxed for 1 hour resulting in a colour change from pale blue to green. The dropwise addition of a solution of 44.2 mg (0.54 mmol) NaSCN in 10 ml CH<sub>3</sub>CN results in the formation of a white precipitate. After its removal by filtration the volume of the green solution is reduced to 15 ml. Vapour diffusion of Et<sub>2</sub>O gives green crystals of 7 (77.6 mg, 25%). Anal. found C, 55.29; H, 4.01; N, 20.27; S, 7.02%; C<sub>40</sub>H<sub>32</sub>N<sub>12</sub>Ni<sub>2</sub> requires C, 55.72; H, 3.74; N, 19.49; S, 7.44. IR (KBr): ν = 2954, 2931, 2916, 2854, 2102 (NCS), 2089 (NCS), 1603 (C=N), 1594, 1575, 1469, 1447, 1330, 1253, 1212, 1060, 1006, 969, 926, 892, 782, 751, 715, 694, 658, 476. λ<sub>max</sub>/nm (MeCN) (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 596 (51), 907 (9).

### X-ray Crystallography

The X-ray data were collected on Bruker SMART area detector {[4<sup>Me</sup>(H<sub>2</sub>O)]<sub>∞</sub>} and Bruker Kappa Apex II area detector {[4<sup>Ph</sup>(CH<sub>3</sub>OH)<sub>2</sub>]<sub>2</sub> and 7·0.5MeCN} diffractometers (λ = 0.71073 Å) and the structures solved and refined using SHELXS [22] and SHELXL, [23] respectively. CCDC reference numbers 610306, 610307 and 610994 respectively.

Crystal data for [4<sup>Me</sup>(H<sub>2</sub>O)]<sub>∞</sub>, (colourless block, 110 K): C<sub>6</sub>H<sub>8</sub>N<sub>3</sub>O<sub>3</sub>Na, M = 193.14, hexagonal, space group P6<sub>1</sub>, a = 8.5737(7), b = 8.5737(7), c = 21.501(2) Å, U = 1368.8(2) Å<sup>3</sup>, Z = 6, μ = 0.152 mm<sup>-1</sup>, 8230 reflections collected. Intensity statistics ((E<sup>2</sup> - 1) = 0.608) strongly suggested a twinned acentric structure. Not unexpectedly refinement in P6<sub>1</sub> died at R1 = 0.15. Introduction of twinning (twin law: 0 1 0/1 0 0/0 0 -1) led to R1 = 0.033 on observed data with a twin component of 0.449(3). Addition of inversion twinning did not improve R1 or wR2. Two peaks of approximately equal electron density were located on the bridging oxygen atom. These peaks were included as hydrogen atoms with restraints on distances and thermal parameters. R1 = 0.0292 [for 1849 F > 4σ(F); wR2 = 0.0765 and goodness of fit = 0.943 for all 1849 independent F<sup>2</sup>; 128 parameters; absolute structure parameter 0.1(5)].

Crystal data for [4<sup>Ph</sup>(CH<sub>3</sub>OH)<sub>2</sub>]<sub>2</sub>, (colourless block, 87 K): C<sub>36</sub>H<sub>36</sub>N<sub>6</sub>Na<sub>2</sub>O<sub>8</sub>, M = 726.70, triclinic, space group P-1, a = 8.1097(9), b = 11.3710(5), c = 11.3935(5) Å, U = 892.06(11) Å<sup>3</sup>, Z = 1, μ = 0.117 mm<sup>-1</sup>, 20904 reflections collected. The hydrogen atom on each of the methanol oxygen atoms was located from difference maps and refined freely. R1 = 0.0302 [for 3633 F > 4σ(F); wR2 = 0.0826 and goodness of fit = 1.049 for all 3633 independent F<sup>2</sup>; 245 parameters].

Crystal data for 7·0.5MeCN, (green block, 89 K): C<sub>41</sub>H<sub>33.50</sub>N<sub>12.50</sub>Ni<sub>2</sub>S<sub>2</sub>, M = 882.84, orthorhombic, space group Fdd2, a = 30.8289(7), b = 39.5999(10), c = 12.9929(3) Å, U = 15862.0(7) Å<sup>3</sup>, Z = 16, μ = 1.104 mm<sup>-1</sup>, 82404 reflections collected. R1 = 0.0240 [for 8111 F > 4σ(F); wR2 = 0.0601 and goodness of fit = 1.065 for all 8111 independent F<sup>2</sup>; 544 parameters; absolute structure parameter 0.005(7)].

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### References

- [1] Beckmann, U.; Brooker, S. *Coord. Chem. Rev.* **2003**, *245*, 17.
- [2] For example: Prins, R.; Birker, P.J.M.L.; Haasnoot, J.G.; Verschoor, G.C.; Reedijk, J.; *Inorg. Chem.*, **1985**, *24*, 4128; Antolini, L.; Fabretti, A.C.; Gatteschi, D.; Giusti, A.; Sessoli, R.; *Inorg. Chem.*, **1990**, *29*, 143; Krober, J.; Codjovi, E.; Kahn, O.; Groliere, F.; Jay, C. *J. Am. Chem. Soc.*, **1993**, *115*, 9810; van Koningsbruggen, P.J.; Gatteschi, D.; de Graaff, R.A.G.; Haasnoot, J.G.; Reedijk, J.; Zanchini C. *Inorg. Chem.*, **1995**, *34*, 5175; Garcia, Y.; van Koningsbruggen, P.J.; Bravic, G.; Guionneau, P.; Chasseau, D.; Cascarano, G.L.; Moscovici, J.; Lambert, K.; Michalowicz, A.; Kahn, O. *Inorg. Chem.*, **1997**, *36*, 6357; van Koningsbruggen, P.J.; Haasnoot, J.G.; Kooijman, H.; Reedijk, J.; Spek, A.L. *Inorg. Chem.*, **1997**, *36*, 2487; Kahn, O. *Chem. Br.*, **1999**, *2*, 24; Garcia, Y.; Kahn, O.; Rabardel, L.; Chansou, B.; Salmon, L.; Tuchagues, J.P. *Inorg. Chem.*, **1999**, *38*, 4663; Stassen, A.F.; d. V. M., van Koningsbruggen P. J.; Renz, F.; Ensling, J.; Kooijman, H.; Spek, A. L.; Haasnoot, J.G.; Gütlich, P.; Reedijk, J. *Eur. J. Inorg. Chem.*, **2000**, 2231; Haasnoot, J. G. *Coord. Chem. Rev.*, **2000**, *131*, 200–202; Klingele, M. H.; Brooker, S. *Coord. Chem. Rev.*, **2003**, *241*, 119; Klingele, M.H.; Moubaraki, B.; Cashion, J. D.; Murray, K. S.; Brooker, S. *Chem. Commun.*, **2005**, 987.
- [3] For example: Browne, W. R.; O'Connor, C. M.; Hughes, H. P.; Hage, R.; Walter, O.; Doering, M.; Gallagher, J. F.; Vos, J. G. *J. Chem. Soc., Dalton Trans.* **2002**, 4048.
- [4] Brooker, S.; Davidson, T. C.; Hay, S. J.; Kelly, R. J.; Kennepohl, D. K.; Plioger, P. G.; Moubaraki, B.; Murray, K. S.; Bill, E.; Bothe, E. *Coord. Chem. Rev.* **2001**, *3*, 216–217.
- [5] Brooker, S. *Eur. J. Inorg. Chem.* **2002**, 2535.
- [6] Alonso, J. M.; Martin, M. R.; de Mendoza, J.; Torres, T. *Heterocycles* **1987**, *26*, 989.
- [7] Duro, J. A.; Ontoria, J. M.; Sastre, A.; Schafer, W.; Torres, T. *J. Chem. Soc., Dalton Trans.* **1993**, 2595; Cabezon, B.; Sastre, A.; Torres, T.; Schafer, W.; Borrás-Almenar, J. J.; Coronado, E. *J. Chem. Soc., Dalton Trans.*, **1995**, 2305; Cabezon, B.; Irurzun,

- M.; Torres, T.; Vazquez, P. *Tetrahedron Lett.*, **1998**, 39, 1067; Nicolau, M.; Cabezón B.; Torres, T. *J. Org. Chem.*, **2001**, 66, 89; Rodríguez-Morgade, M.S.; Cabezón, B.; Esperanza, S.; Torres, T. *Chem. Eur. J.*, **2001**, 7, 2407.
- [8] Alcalde, E.; Alemany, M.; Perez-Garcia, L.; Rodríguez, M. L. *J. Chem. Soc., Chem. Commun.* **1995**, 1239, Alcalde, E.; Gisbert, M.; Alvarez-Rua, C.; Garcia-Granda, S. *Tetrahedron*, **1996**, 52, 15189; Alcalde, E.; Mesquida, N.; Perez-Garcia, L.; Ramos, S.; Alemany M.; Rodríguez, M. L. *Chem. Eur. J.*, **2002**, 8, 474.
- [9] Beckmann, U.; Brooker, S.; Depree, C. V.; Ewing, J. D.; Moubaraki, B.; Murray, S. *Dalton Trans.* **2003**, 7, 1308.
- [10] Beckmann, U.; Ewing, J. D.; Brooker, S. *Chem. Commun.* **2003**, 1690.
- [11] Depree, C. V.; Beckmann, U.; Heslop, K.; Brooker, S. *Dalton Trans.* **2003**, 3071.
- [12] Martínez-Díaz, M. V.; de Mendoza, J.; Santos, F.; Torres, T. *Tetrahedron: Asymmetry* **1994**, 5, 1291.
- [13] de Mendoza, J.; Ontoria, J. M.; Ortega, M. C.; Torres, T. *Synthesis* **1992**, 398.
- [14] Orihuela, S.; Sanchez, M. P.; Quiros, M.; Molina, J.; Faure, R. *J. Mol. Struct.* **1997**, 415, 285.
- [15] Brandt, C. D.; Plieger, P. G.; Kelly, R. J.; de Geest, D. J.; Kennepohl, D. K.; Iremonger, S. S.; Brooker, S. *Inorg. Chim. Acta* **2004**, 357, 4265.
- [16] Nakamoto, K. Infrared and raman spectra of inorganic coordination compounds. Part A., John Wiley & Sons, Inc. **1997**.
- [17] Di Vaira, M.; Sacconi, L. *Chem. Commun.* **1969**, 10, Di Vaira, M.; *J. Chem. Soc. A*, 1971, 148.
- [18] Sacconi, L.; Morassi, R. *J. Chem. Soc. A* **1969**, 2904.
- [19] Keij, F. S.; deGraaff, R. A. G.; Haasnoot, J. G.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1984**, 2093, Klingele, M.H.; Boyd, P.D.W.; Moubaraki, B.; Murray, K.S.; Brooker, S. *Eur. J. Inorg. Chem.*, 2005, 910.
- [20] Kitchen, J. A.; Noble, A.; Weitzer, M.; Hellyer, R. M.; White, N. G.; Brooker, S., *unpublished results*.
- [21] Brooker, S.; Kelly, R. J.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1994**, 487, Brooker, S.; Kelly, R.J.; *J. Chem. Soc., Dalton Trans.*, 1996, 211.
- [22] Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, 46, 467, Sheldrick, G. M.; *Methods Enzymol.*, 1997, 276, 628.
- [23] Sheldrick, G. M.; Schneider, R. *Methods Enzymol.* **1997**, 277, 319.