

# Chain polymeric complexes of some first-series transition-metal ions with *N,N,N',N'*-tetra-acetyl-1,4-diaminobutane

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We dedicate this paper to Professor F.A. Cotton to mark the occasion of his 70th birthday.

## Abstract

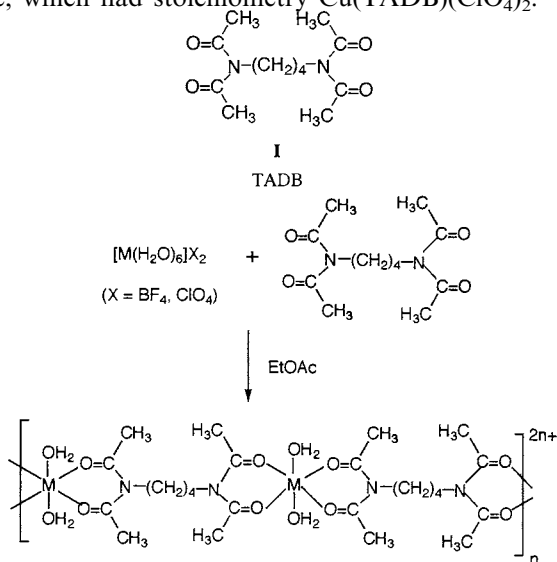
The preparations are reported of the compounds  $[M(\text{TADB})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  (where TADB = *N,N,N',N'*-tetra-acetyl-1,4-diaminobutane, and M = Mn, Co, Ni and Zn), and also of the analogous tetrafluoroborate salts with M = Mn, Co, Cu and Zn, and the complex  $\text{Cu}(\text{TADB})(\text{ClO}_4)_2$ . Crystals of  $[\text{Zn}(\text{TADB})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  are monoclinic,  $P2_1/n$ , with  $a = 7.3735(2)$ ,  $b = 12.4954(5)$ ,  $c = 12.0313(5)$  Å,  $\beta = 100.581(4)^\circ$ , and  $Z = 2$ . Each zinc centre is coordinated to two *trans*-disposed aqua ligands and two chelating diacetamide units, one from each of two different TADB ligands, which, in turn bridge neighbouring zinc centres so as to generate cationic polymeric chains. X-ray powder diffraction studies show that, except for the copper(II) compounds, the other complexes are isostructural with the zinc complex. X-band EPR spectral results for the manganese(II) complexes and for samples of the other compounds 'doped' with small amounts of manganese(II) are also given. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Crystal structure; Polymeric complex; EPR

## 1. Introduction

Recently we reported on the propensity of the alkane-bridged bis(amides),  $\text{CH}_3\text{CONH}(\text{CH}_2)_n\text{NHCOCH}_3$  ( $n = 2, 4$  or  $6$ ) to link first-row transition-metal ions such as manganese(II) and cobalt(II) into network arrays [1]. The facility with which these networks are formed encouraged us to study some related tetra-acetylalkanediamine ligands as these possess the potential for chelate formation, as distinct from monodentate coordination, at each end of the extended ligand system. Reaction of *N,N,N',N'*-tetra-acetyl-1,4-diaminobutane,  $(\text{CH}_3\text{CO})_2\text{N}(\text{CH}_2)_4\text{N}(\text{COCH}_3)_2$  (I, TADB) with the hydrated metal perchlorates or tetrafluoroborates of the series  $\text{Mn}^{\text{II}}$  to  $\text{Zn}^{\text{II}}$  in ethyl acetate resulted in the formation of complexes of stoichiometry  $[M(\text{TADB})(\text{H}_2\text{O})_2]X_2$  ( $X = \text{ClO}_4$  or  $\text{BF}_4$ ) (Scheme 1)

except for the product formed by copper(II) perchlorate, which had stoichiometry  $\text{Cu}(\text{TADB})(\text{ClO}_4)_2$ .



Scheme 1.

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Table 1  
Colours, yields and analytical data for the complexes

Complex	Colour	Yield (%)	Analysis (%) <sup>a</sup>		
			C	H	N
[Mn(TADB)(H <sub>2</sub> O) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	White	72	26.3(26.4)	4.6(4.4)	5.0(5.1)
[Mn(TADB)(H <sub>2</sub> O) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	White	76	27.8(27.7)	4.8(4.6)	5.2(5.4)
[Co(TADB)(H <sub>2</sub> O) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	Pink	88	26.3(26.2)	4.5(4.4)	5.1(5.1)
[Co(TADB)(H <sub>2</sub> O) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	Pink	89	27.5(27.5)	4.6(4.6)	5.2(5.3)
[Ni(TADB)(H <sub>2</sub> O) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	Green	82	25.9(26.2)	4.5(4.4)	4.9(5.1)
Cu(TADB)(ClO <sub>4</sub> ) <sub>2</sub>	Light blue	80	27.6(27.8)	4.2(3.9)	5.2(5.4)
[Cu(TADB)(H <sub>2</sub> O) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	Blue green	82	26.7(27.2)	4.6(4.6)	5.3(5.3)
[Zn(TADB)(H <sub>2</sub> O) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	White	73	26.1(25.9)	4.4(4.4)	5.2(5.0)
[Zn(TADB)(H <sub>2</sub> O) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	White	79	27.2(27.1)	4.6(4.6)	5.3(5.3)

<sup>a</sup> Calculated values in parentheses.

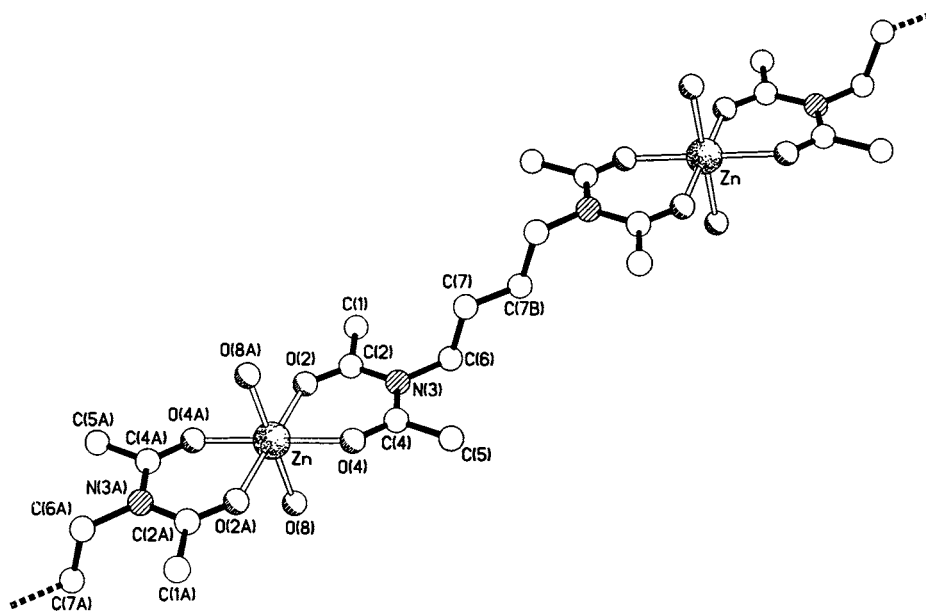


Fig. 1. Part of one of the polymeric chains present in the structure of **1**.

We report here the single-crystal X-ray characterisation of one representative member of this series, [Zn(TADB)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**), and the results of some spectroscopic studies on the other compounds.

## 2. Results and discussion

The TADB complexes isolated in this work (Table 1) were readily obtained in relatively high yields. X-ray powder diffraction studies showed that, except for the copper(II) compounds, all the complexes (both perchlorates and tetrafluoroborates) form an isostructural series. The solid-state electronic spectra of the cobalt(II) and nickel(II) compounds are typical of complexes with an essentially octahedral environment of O-donor ligands (with  $\lambda = 9500 \text{ cm}^{-1}$ ), both in terms of the observed band energies [2,3] (see Section 3) and low band

intensity. The observed average  $\Delta$  value of  $9500 \text{ cm}^{-1}$  for the [M(TADB)(H<sub>2</sub>O)<sub>2</sub>] (M = Co, Ni) chromophores points to a  $\Delta$  value of ca.  $10000 \text{ cm}^{-1}$  for TADB, a value very similar to that reported [4] for diacetamide, (CH<sub>3</sub>CO)<sub>2</sub>NH.

Our main interest, however, was to establish the way in which the TADB ligand propagates the long-range structures of these complexes, for comparison with those formed by the previously described bisamide ligands [1]. Accordingly we have determined, by X-ray diffraction methods, the crystal structure of a representative member of the series, [Zn(TADB)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**).

### 2.1. Structure of [Zn(TADB)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**)

As anticipated, the X-ray analysis confirmed that TADB acts as a bridging, bischelating ligand to form

approximately linear, cationic polymeric chains  $\{[\text{Zn}(\text{TADB})(\text{H}_2\text{O})_2]\}_n^{2+}$  (Fig. 1).

The geometry at each zinc centre is slightly distorted octahedral with *cis* angles ranging between 80.6(1) and 99.4(1)°, with, as expected, the acute angle being associated with the bite of the chelate ring. As the zinc atom is positioned on a crystallographic inversion centre, all the *trans* angles are 180°. The aqua⋯aqua [O(8)⋯O(8A)] vector is inclined by 87.5° to the equatorial plane, the inclination from orthogonal being in a direction along the O(4)–Zn–O(2A) bisector.

There is a small, but significant, difference between the axial Zn–aqua bond lengths (2.095(5) Å) and the equatorial Zn–O bonds formed to the carbonyl oxygen atoms [2.037(3) Å to O(2) and 2.045(4) Å to O(4)]. The effects of this asymmetry are seen in the manganese(II) EPR spectra, as discussed below. It is interesting to note that in the related, though not directly analogous, complexes formed by diacetamide with cobalt(II) chloride [5] and magnesium perchlorate [6] the bonds to the aqua ligand are shorter than those to the carbonyl oxygen atoms.

The six-membered chelate ring is slightly folded with the zinc atom lying 0.13 Å out of the plane of the other five atoms, which are coplanar to within 0.02 Å. The N–(CH<sub>2</sub>)<sub>4</sub>–N backbone of the TADB ligand is essentially planar (there is an inversion centre in the middle of the C(7)–C(7B) bond) and is inclined almost orthogonally (87°) to the O(2)C(2)N(3)C(4)O(4) plane.

The polymer chains propagate along the crystallographic 101 direction and are cross-linked by hydrogen bonds between the aqua ligands and the perchlorate

anions. These interactions produce corrugated sheets (ca. 50° zigzag) of molecules as illustrated in Fig. 2. Adjacent sheets are stacked ‘peak-in-trough’ but with no significant inter-sheet interactions.

As stated earlier, X-ray powder diffraction studies showed that, except for the copper(II) compounds, all the complexes form an isostructural series. To illustrate this, Fig. 3 shows a comparison of the powder patterns of  $[\text{M}(\text{TADB})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  (M = Mn and Ni) with the pattern calculated from the structure of  $[\text{Zn}(\text{TADB})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  (1) determined by the single-crystal study.

## 2.2. EPR spectra

Although the deviations from full octahedral symmetry around the metal ions are too small to be seen in the electronic spectra of the solid cobalt(II) and nickel(II) complexes, the X-band EPR spectrum of solid  $[\text{Mn}(\text{TADB})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  clearly shows the distortion. While the strongest bands are near  $g_{\text{eff}} = 2$ , other bands, due to the zero-field splitting (ZFS) arising from the departure from  $O_h$  symmetry, are observed over the range 0–700 mT (Fig. 4(A)), with considerable intensity at low field.

Dilution (nominal 1%) of the manganese complex in the isomorphous cobalt, nickel or zinc complexes gave a set of virtually identical spectra, but with resolved manganese nuclear hyperfine structure (Fig. 4(B)). This resolved structure falls entirely under the broad bands observed for the undiluted compound, showing that there is no serious exchange in the latter. The typical

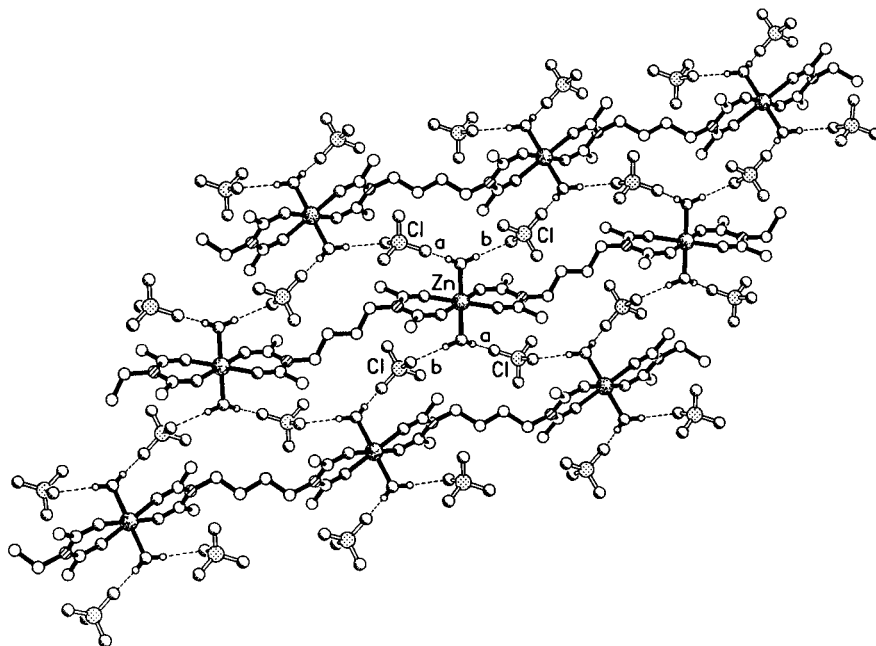


Fig. 2. Part of one of the continuous sheets formed by cross-linking via O–H⋯O hydrogen bonds between the aqua ligands and the perchlorate anions. The hydrogen-bonding geometries are: (a) O⋯O 2.78, H⋯O 1.88 Å, O–H⋯O angle 175°; (b) O⋯O 2.94, H⋯O 2.12 Å, O–H⋯O angle 150°.

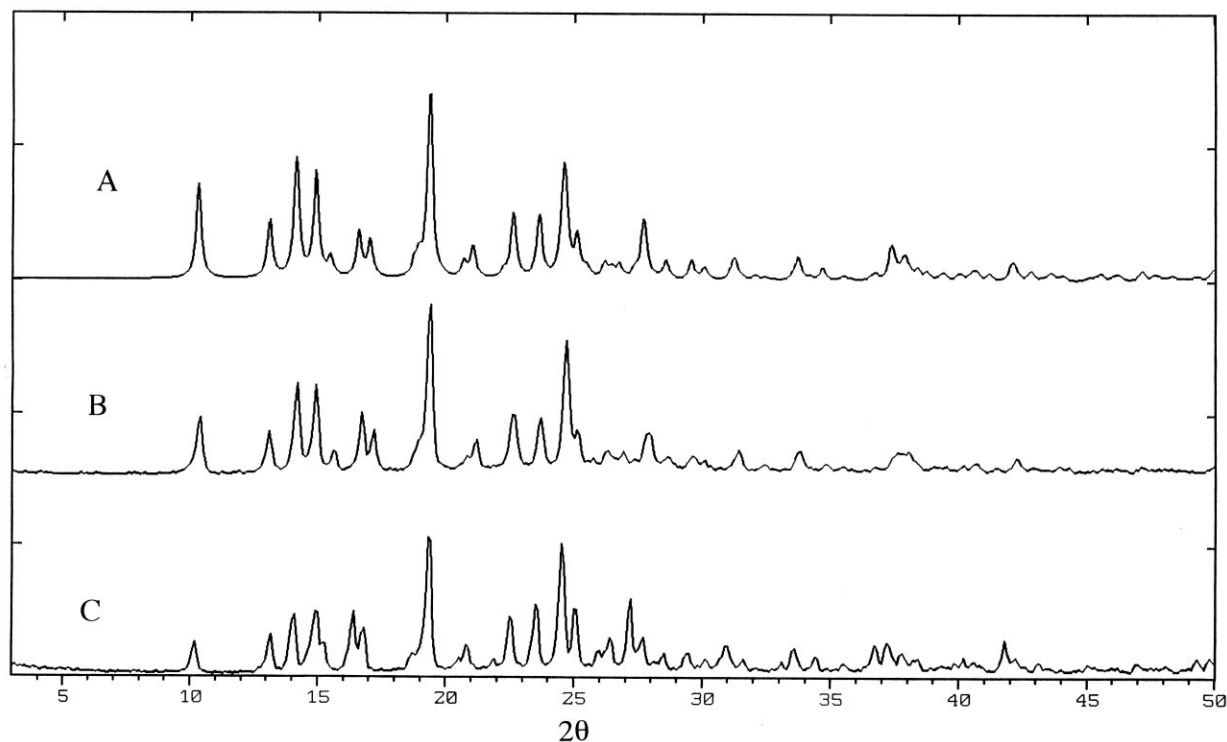


Fig. 3. (A) Calculated powder diffraction pattern from the single-crystal structure of  $[\text{Zn}(\text{TADB})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ . (B) Observed powder diffraction pattern of  $[\text{Ni}(\text{TADB})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ . (C) Observed powder diffraction pattern of  $[\text{Mn}(\text{TADB})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ .

manganese hyperfine pattern confirmed the existence of the weak band near 700 mT (Fig. 4(B)).

The complicated, overlapping band structure in these X-band spectra precluded derivation of the ZFS parameters  $D$  and  $E$ . Consequently, to obtain an estimate of these parameters, and hence a comparison with related compounds, measurements on the zinc complex doped with a nominal 1% of the manganese(II) compound were made at Q-band frequency. As expected, the main intensity was centred near to 1200 mT, but bands were present between ca. 860 and 1580 mT (Fig. 5). This is consistent with a  $D$  value of about  $0.085 \text{ cm}^{-1}$ , with the outermost bands assigned as the lowest and highest transitions, respectively, along the  $z$ -axis.

This observed  $D$  value falls near the centre of the range ( $0.077\text{--}0.098 \text{ cm}^{-1}$ ) obtained [7,8] for a series of manganese-doped complexes of diacetamide, having chromophores of the type  $[\text{M}(\text{diacetamide})_2(\text{H}_2\text{O})_2]^{2+}$ . Where it was possible to determine the sign of  $D$  in those compounds it was always positive, pointing to an axial elongation of the crystal field. Assuming that the major axis of the  $D$  tensor lies along, or close to, the direction of the  $\text{M}(\text{OH}_2)_2$  bonds, it seems likely that this is also the case in the TADB complexes as the  $\text{Zn}\text{--}\text{O}$  bonds to the aqua ligands ( $2.095(5) \text{ \AA}$ ) are longer than those to the oxygen atoms of the TADB ligands ( $2.037(3)$  and  $2.045(4) \text{ \AA}$ ). Such a high  $D$  value is also in agreement with the relatively strong ligand field (for an

O-donor ligand) generated by TADB shown by the electronic spectral results for the cobalt(II) and nickel(II) complexes.

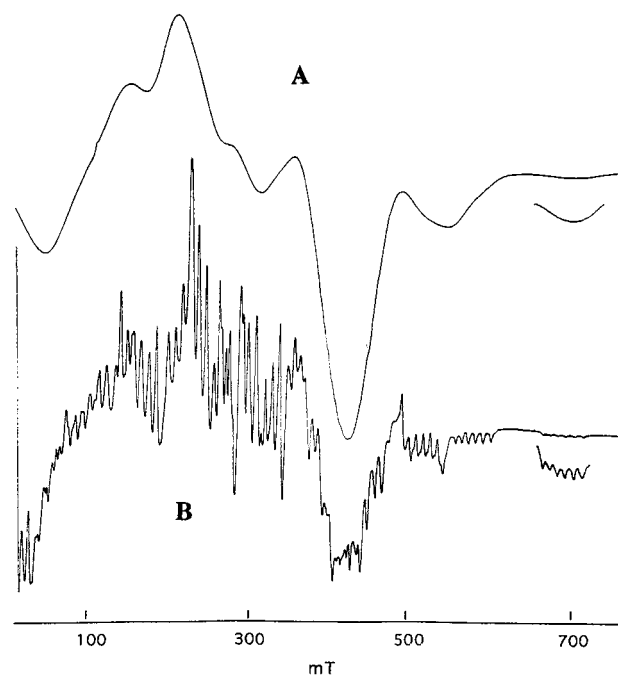


Fig. 4. X-band EPR spectra at room temperature of powdered solid samples of: (A)  $[\text{Mn}(\text{TADB})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ ; (B)  $[\text{Zn}(\text{Mn})(\text{TADB})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ , nominal 1% Mn doping.

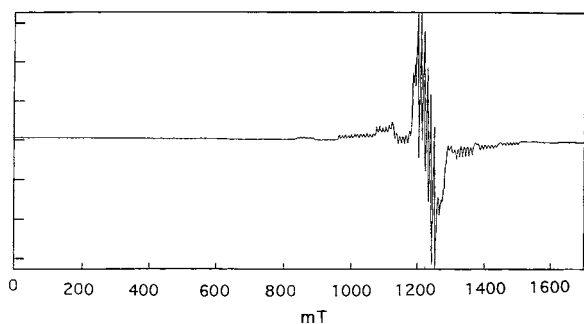


Fig. 5. Q-band EPR spectrum at room temperature of a powdered solid sample of  $[\text{Zn}(\text{Mn})(\text{TADB})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ , nominal 1% Mn doping.

The rhombic distortion of the metal ion coordination geometry revealed by the X-ray structural study on **1** is also evident from the manganese(II) EPR spectra. Within the limits of the spectral resolution, the separation of what appear to be the outermost transitions along the  $x$  and  $y$  axes suggest a value of about 0.11–0.12 for  $\lambda$  ( $E/D$ ), that is an  $E$  value of ca.  $0.01 \text{ cm}^{-1}$ . This value of  $E$  is higher than those observed previously [7,8] for complexes of diacetamide, which afforded  $E$  values in the range  $3 \times 10^{-4}$ – $7 \times 10^{-3} \text{ cm}^{-1}$ .

In conclusion, the present study has established the ease with which the TADB ligand facilitates polymer formation by harnessing its effective chelating ability at each end of the extended molecule. The present results offer the prospect for the creation of further, novel species such as those that would result from tris-chelation at an octahedrally coordinated metal centre, or the generation of an even higher coordination number by the use of e.g. lanthanide ions. Moreover, by variation of the length and nature of the linking group between the chelating bis(amide) units, these types of complex provide useful probes for studying the electronic behaviour of a range of species via appropriate physical techniques, such as the EPR results reported here.

### 3. Experimental

#### 3.1. Preparation of the compounds

##### 3.1.1. $N,N,N',N'$ -tetra-acetyl-1,4-diaminobutane (TADB)

Acetic anhydride ( $100 \text{ cm}^3$ ) was added dropwise to 1,4-diaminobutane (0.1 mol) with continuous stirring. The resulting solution was refluxed for 18 h and then concentrated to ca.  $80 \text{ cm}^3$  and allowed to cool. The white, crystalline product was collected and recrystallized from methanol (82% yield). Anal. Found: C, 56.3; H, 8.2; N, 11.0. Calc. for  $\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_4$ : C, 56.2; H, 7.9; N, 10.9%. The nature of the product was also con-

firmed by the single-crystal X-ray analysis of its zinc perchlorate complex.

#### 3.1.2. Metal complexes

**Caution!** Although we did not observe any explosive behaviour with any of the perchlorate compounds described below, all metal perchlorates must be regarded as potentially explosive and appropriate safety measures must be taken (see, for example Ref. [9]).

The metal complexes were all prepared by the same general method. A solution of the respective, hydrated metal(II) perchlorate or tetrafluoroborate (0.2 mmol) in hot ethyl acetate ( $3 \text{ cm}^3$ ) was mixed with a solution of TADB (0.3 mmol) also in hot ethyl acetate ( $4 \text{ cm}^3$ ) and then heated to boiling for a short time. The solid complex that separated was filtered off, washed with diethyl ether and dried in vacuo. The complexes obtained are listed in Table 1, together with the colours, yields and analytical data (Scientific Analysis and Consultancy Service, University of North London). The complexes are somewhat hygroscopic.

The crystals of  $[\text{Zn}(\text{TADB})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  used for X-ray structural determination were obtained using a more dilute solution (a total of  $15 \text{ cm}^3$  of solvent) and formed over a period of ca. 3 h.

### 3.2. Spectroscopy

#### 3.2.1. Electronic spectra

Electronic spectra of the solid compounds were measured by the reflectance method on a Beckman DK2 spectrometer. Band energies ( $\text{cm}^{-1}$ ):  $[\text{Co}(\text{TADB})-$

Table 2  
Crystallographic data for compound **1**

Formula	$[\text{C}_{12}\text{H}_{24}\text{N}_2\text{O}_6\text{Zn}](\text{ClO}_4)_2$
Formula weight	556.60
Crystal system	Monoclinic
Crystal size (mm)	$0.20 \times 0.20 \times 0.10$
Space group	$P2_1/n$
$a$ (Å)	7.3735(2)
$b$ (Å)	12.4954(5)
$c$ (Å)	12.0313(5)
$\beta$ (°)	100.581(4)
$V$ (Å <sup>3</sup> )	1089.65(7)
$Z$	2
$D_{\text{calc.}}$ ( $\text{g cm}^{-3}$ )	1.696
$\lambda$ (Å)	1.54178
$\mu$ ( $\text{mm}^{-1}$ )	4.491
$\theta$ Range (°)	5.15–55.98
$F(000)$	572
Measured reflections	1760
Unique reflections	1620
Observed reflections [ $F > 4\sigma(F)$ ]	1308
Data/restraints/parameters	1620/2/151
Mean, max $\Delta/\sigma$ ratio	0.000, 0.001
Largest diff. peak/hole ( $\text{e Å}^{-3}$ )	0.724, $-0.990$
$R_1, wR_2$	0.0577, 0.1473

Table 3  
Selected bond lengths (Å) and angles (°) for compound **1**

Bond lengths			
Zn–O(2)	2.037(3)	Zn–O(4)	2.045(4)
Zn–O(8)	2.095(5)	C(2)–O(2)	1.225(6)
C(4)–O(4)	1.223(6)	C(2)–N(3)	1.406(7)
N(3)–C(4)	1.394(7)		
Bond angles			
O(2)–Zn–O(2A)	180	O(2)–Zn–O(4)	80.6(1)
O(2)–Zn–O(4A)	99.4(1)	O(2)–Zn–O(8)	90.9(2)
O(2)–Zn–O(8A)	89.1(2)	O(4)–Zn–O(4A)	180
O(4)–Zn–O(8)	87.8(2)	O(4)–Zn–O(8A)	92.2(2)
O(8)–Zn–O(8A)	180		

(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> 8700 (<sup>4</sup>T<sub>2g</sub>), 18 700 (<sup>4</sup>A<sub>2g</sub>), 20 400 (<sup>4</sup>T<sub>1g</sub>, P); [Co(TADB)(H<sub>2</sub>O)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> 8700 (<sup>4</sup>T<sub>2g</sub>), 18 700 (<sup>4</sup>A<sub>2g</sub>), 20 400 (<sup>4</sup>T<sub>1g</sub>, P); [Ni(TADB)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> 9500 (<sup>3</sup>T<sub>2g</sub>), 14 700 (<sup>3</sup>T<sub>1g</sub>, F), 24 900 (<sup>3</sup>T<sub>1g</sub>, P).

### 3.2.2. EPR spectra

The EPR spectra were measured on powdered solid samples at room temperature. The X-band spectra were obtained using a Varian E12 X-band spectrometer. The Q-band EPR measurements were made at the EPSRC c.w. EPR Service Centre, Department of Chemistry, University of Manchester, on a Bruker ESP300E spectrometer fitted with an ER5106QT resonator and a Bruker ER035M NMR gaussmeter and an EIP model 588C microwave pulse counter for magnetic field and microwave frequency calibration, respectively. The Mn(II) ‘doped’ samples were obtained by preparing the host complex but using a solution of the metal salt to which a nominal 1% ‘impurity’ of manganese(II) perchlorate or tetrafluoroborate, respectively, had been added.

### 3.2.3. IR spectra

IR spectra (cm<sup>-1</sup>, Nujol mulls) of [M(TADB)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (M = Co, Ni, Zn): Co 3443br, 1709, 1686, 1623, 1565, 1341, 1288, 1176, 1093br, 1033, 972, 957, 877; Ni 3405br, 1710br, 1635, 1559, 1343, 1288, 1264, 1174, 1090br, 1024, 970, 878; Zn 3517, 3446, 1710, 1693, 1625, 1425, 1348, 1290, 1270, 1180, 1093br, 1039, 974, 958, 881.

### 3.3. X-ray crystallography

A summary of the crystal data and of the data collection and refinement parameters for [Zn(TADB)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**) is given in Table 2. Data were measured on a Siemens P4/PC diffractometer using Cu–K<sub>α</sub> radiation. The data were corrected for Lorentz and polarisation effects and for absorption

(ellipsoidal). The structure was solved by direct methods and refined by full-matrix least-squares based on *F*<sup>2</sup>. The non-hydrogen atoms were refined anisotropically. The C–H hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, *U*(H) = 1.2*U*<sub>eq</sub>(C), [*U*(H) = 1.5*U*<sub>eq</sub>(C–Me)], and allowed to ride on their parent atoms. Computations were carried out using the SHELXTL PC program system [10]. Selected bond lengths and angles for **1** are given in Table 3.

The X-ray powder diffraction studies were carried out using a Siemens D500 powder diffractometer, with Cu–K<sub>α</sub> radiation, operating in reflecting mode with a diffracted beam monochromator.

## 4. Supplementary material

Full crystallographic details have been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 134236). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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## References

- [1] D.M.L. Goodgame, D.A. Grachvogel, I. Hussain, A.J.P. White, D.J. Williams, *Inorg. Chem.* 38 (1999) 2057.
- [2] A.D. Liehr, *J. Phys. Chem.* 67 (1963) 1314.
- [3] A.D. Liehr, *Ann. Phys.* 6 (1959) 134.
- [4] C.S. Kraihanzel, S.C. Grenda, *Inorg. Chem.* 4 (1965) 2057.
- [5] T.S. Khodashova, V.P. Nikolaev, M.A. Porai-Koshits, L.A. Butman, I.I. Tabidze, G.V. Tsintsadze, *Koord. Khim.* 12 (1986) 128.
- [6] P.S. Gentile, J.G. White, M.P. Dinstein, D.D. Bray, *Inorg. Chim. Acta* 21 (1977) 141.
- [7] M. Goodgame, I. Hussain, *Inorg. Chim. Acta* 174 (1990) 245.
- [8] M. Goodgame, I. Hussain, *Inorg. Chim. Acta* 229 (1995) 165.
- [9] W.C. Wolsey, *J. Chem. Educ.* 50 (1973) A335.
- [10] SHELXTL-PC version 5.03, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994.