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Mono-, di- and poly-nuclear transition-metal complexes of a bis(tridentate) ligand: towards *p*-phenylenediamine-bridged co-ordination polymers

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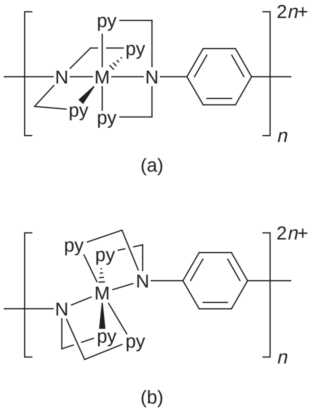
The bis(tridentate) ligand *N*,*N*,*N'*,*N'*-tetrakis(2-pyridylmethyl)benzene-1,4-diamine (1,4-tpbd) is multifunctional in that mono-, di- and poly-nuclear transition-metal complexes as well as bis-co-ordinated complexes can be prepared. A prototype example of each class of complex has been characterized. In [$ZnCl_2$(2,4-tpbd)] the 1,4-tpbd is co-ordinated *via* only one of its tridentate ends. Both ends of 1,4-tpbd are bound in a dipalladium complex. [Pd_2Cl_2(1,4-tpbd)][$PdCl_3$(dmso)]$_2$. This structure constitutes the first example of a crystal structure of the counter anion [$PdCl_3$(dmso)]$^-$. The chloride salt of the [Pd_2Cl_2(tpbd)]$^{2+}$ cation has also been isolated. In the structures of both [$ZnCl_2$(1,4-tpbd)] and [Pd_2Cl_2(tpbd)]$^{2+}$ quinoid character of the benzene linker of the 1,4-tpbd is evident. The compound [Ru(1,4-tpbd)$_2$][PF_6]$_2$ is an example of a bis-co-ordinated complex. One tridentate end of each ligand is co-ordinated to the ruthenium(II) ion while the other end is unco-ordinated. These three contrasting complexes demonstrate the versatility of 1,4-tpbd as a ligand for transition-metal complexes and the series represent the structural elements required for the construction of homo- and hetero-nuclear co-ordination oligo- or poly-mers. The compositions of the products isolated from the reaction of 1,4-tpbd with iron and nickel are consistent with the polymeric formulations [M(1,4-tpbd)]$_n$A$_{2n}$ (M = Fe, A = Cl; M = Ni, A = NO_3).

The last decade has witnessed a surge of interest in the discovery of simple building blocks capable of forming specific molecular arrays under certain chemical conditions.[1] For example, the addition of a specific metal ion to appropriate ligands may induce the formation of one- and two-dimensional polymers or framework structures as a consequence of the constraints induced by co-ordination.[2] The search for appropriate organic building blocks for the construction of one-dimensional co-ordination polymers has led us to investigate tetra-*N*-functionalized *p*-phenylenediamines as potential bis(tridentate) bridging ligands. We have recently reported the preparation and characterization of the new potentially redox-active hexadentate *p*-phenylenediamine-based ligand *N*,*N*,*N'*,*N'*-tetrakis(2-pyridylmethylbenzene)-1,4-diamine (1,4-tpbd) and its dicopper complexes with the general formulation [L_2Cu(1,4-tpbd)CuL_2]$^{n+}$ ($L = H_2O$, $n = 4$; L = Cl or NO_3, $n = 0$).[3] The compound 1,4-tpbd is easily oxidized in the presence of the redox-active metal ions Fe^{3+}, Cu^{2+} and Mn^{3+}, and we have characterized, in solution, its one-electron oxidized form, the purple radical cation 1,4-tpbd$^{\cdot+}$, using cyclic voltammetry, ESR and UV/VIS spectroscopy. If 1,4-tpbd is treated with 2 or more equivalents of Cu^{2+} radical formation is suppressed and the dinuclear copper complexes can be isolated. We have found no evidence to suggest any electronic redistribution (*i.e.* the stabilization of a charge-separated state) between the 1,4-tpbd and the copper ions to give, for example, formally mixed-valence radical-bridged complexes of the type [L_2Cu^I-(1,4-tpbd$^{\cdot+}$)$Cu^{II}L_2$]$^{n+}$. In order better to understand the redox behaviour of 1,4-tpbd we have extended this work to include the study of complexes of relatively redox-inert transition-metal ions. Described here are zinc, palladium and ruthenium complexes. Each complex is a prototype for complexes of the following general formulations: [M(1,4-tpbd)L_n]$^{n+}$ [L_nM(1,4-tpbd)ML_n]$^{n+}$ and [(1,4-tpbd)M(1,4-tpbd)]$^{n+}$. This series of complexes demonstrate that 1,4-tpbd shows 'schizodentate' character; co-ordination to transition-metal ions *via* either one or both of 1,4-tpbd's tridentate ends is possible. Thus the elements necessary for the construction of one-dimensional co-ordination polymers using 1,4-tpbd are established. Such a polymer is depicted by Scheme 1 and our initial foray into the preparation of such compounds is also described.



Scheme 1 View of a one-dimensional co-ordination polymer constructed of 1,4-tpbd and a divalent octahedral metal ion: (a) meridional co-ordination of the tridentate chelating end and (b) *trans*-facial co-ordination of the tridentate chelating end (*cis*-facial not shown)

The co-ordination chemistry of 1,4-tpbd may be compared to that of the polypyridyl bis(tridentate) ligands 2,3,5,6-tetra-(2-pyridyl)pyrazine (tppz)[4] and the 'back-to-back' terpy-based systems,[5] *e.g.* 6′,6″-di(2-pyridyl)-2,2′:4′,4″:2″,2‴-quaterpyridine (dpqtpy). To our knowledge crystal structures of metal complexes in which both ends of these ligands are simultaneously bound to a metal ion in either di- or poly-nuclear complexes have been reported in only the case of tppz, for the complexes [Cu_2(tppz)(H_2O)$_4$][ClO_4]$_4$ and [{Zn_2(μ-tppz)(H_2O)Cl(μ-$ZnCl_4$)-(μ-$ZnCl_2$)[μ-$ZnCl_3$(H_2O)]}$_2$][ClO_4]$_4$.[4] Clearly co-ordination of both tppz and dpqtpy results in a meridional arrangement for the tridentate ends of these bis-chelating ligands. By contrast, the presence of a tertiary amine group in 1,4-tpbd gives the

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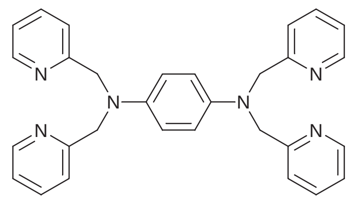
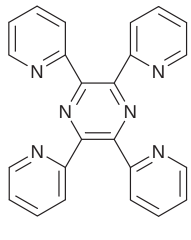
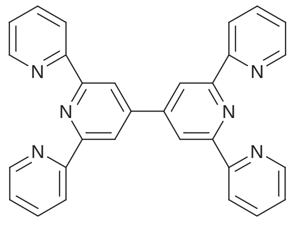


1,4-tpbd



tppz



dpqtpy

potential for both meridional and facial co-ordination geometries. Thus we envision different topologies in dinuclear and polymeric co-ordination complexes of these three linear bis(tridentate) ligands. With the present work we have achieved a more extensive collection of structurally characterized mono- and di-nuclear transition-metal complexes of 1,4-tpbd compared with those known for tppz and dpqtpy.

Experimental

Infrared spectra were measured as KBr discs using a Hitachi 270-30 spectrometer, UV/VIS absorption spectra on a Shimadzu UV-3100 spectrophotometer, EI mass spectra on a Varian MAT311A spectrometer, FAB mass spectra on a Kratos MS-50 spectrometer and NMR spectra on a Bruker AC 250 spectrometer. Elemental analyses were carried out at the microanalytical laboratory of the H.C. Ørsted Institute, Copenhagen. *N*,*N*,*N*′,*N*′-Tetrakis(2-pyridylmethyl)benzene-1,4-diamine was synthesized as reported.[3]

CAUTION: Although no problems were encountered in the preparation of the perchlorate salt, suitable care should be taken when handling such potentially hazardous compounds.

Preparations

Dichloro[*N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethylbenzene)-1,4-diamine]zinc(II), [ZnCl$_2$(1,4-tpbd)]. Zinc chloride (116 mg, 0.864 mmol) in dmso (5 cm^3) was added to a solution of 1,4-tpbd (200 mg, 432 mmol) in dmso (25 cm^3). After 7 d the product was deposited as pale pink crystals. These were collected and dried in vacuum, yield 132 mg, 50% (Found: C, 59.36; H, 4.79; N, 13.77. $C_{30}H_{28}Cl_2N_6Zn$ requires C, 59.18; H, 4.64; N, 13.80%). FAB mass spectrum: *m*/*z* 707.9 {[Zn$_2$Cl$_3$(1,4-tpbd)H$_2$]$^+$, 12}, 671.0 {[Zn$_2$Cl$_2$(1,4-tpbd)H]$^+$, 50} and 635 {[Zn$_2$Cl(1,4-tpbd)]$^+$, 100%}. ^{1}H NMR [(CD$_3$)$_2$SO]: δ 4.64 (s, 8 H, CH$_2$), 6.55 (s, 4 H, C$_6$H$_4$), 7.28 (s, 8 H, py H3, H5) and 7.73 (s, 4 H, py H4); after addition of 3 equivalents of ZnCl$_2$, δ 4.62 (s, 8 H, CH$_2$), 6.73 (s, 4 H, C$_6$H$_4$), 7.52 (m, 8 H, py H3), 7.99 (t, 4 H, py H4, $J = 7.4$) and 8.75 (d, 4 H, py H6, $J = 4.4$ Hz).

Dichloro[*N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)benzene-1,4-diamine]dipalladium(II) trichloro(dimethyl sulfoxide)palladate(II), [Pd$_2$Cl$_2$(1,4-tpbd)][PdCl$_3$(dmso)]$_2$. Palladium(II) chloride (184 mg, 1.04 mmol) was heated in dmso (12 cm^3) at *ca.* 100 °C for 30 min. The compound 1,4-tpbd (120 mg, 0.26 mmol) was added and the solution allowed to stand for 2 weeks, over which time orange crystals, in variable yields, were deposited. These were collected, washed with dmso and dried in vacuum (Found: C, 47.01; H, 4.03; Cl, 18.36. N, 10.85. $C_{17}H_{20}Cl_4N_3O_2Pd_2S$ requires C, 46.34; H, 4.15; Cl, 18.24; N, 10.81%). FAB mass spectrum: *m*/*z* 791 ([*M* + Cl]$^+$, 50), 756 ([*M*]$^+$, 30), 721 ([*M* − Cl]$^+$, 20) and 615 ([*M* − PdCl]$^+$, 75%).

Dichloro[*N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)benzene-1,4-diamine]dipalladium(II) chloride, [Pd$_2$Cl$_2$(1,4-tpbd)]Cl$_2$. Palladium(II) chloride (100 mg, 0.564 mmol) and KCl (84 mg, 1.127 mmol) were heated under reflux for 20 min; 1,4-tpbd (133 mg, 0.282 mmol) was added resulting in immediate precipitation of the light yellow product. Yield 174 mg, 74% (Found: C, 43.01; H, 3.58; N, 10.35. $C_{15}H_{14}Cl_2N_3Pd$ requires C, 43.56; H, 3.41; N, 10.16%). FAB mass spectrum: *m*/*z* 791 {[Pd$_2$Cl$_3$(1,4-tpbd)]$^+$, 36}, 756 {Pd$_2$Cl$_2$(1,4-tpbd)]$^+$, 56}, 721 {[Pd$_2$Cl(1,4-tpbd)]$^+$, 24} and 615 {[PdCl(1,4-tpbd)]$^+$, 51%}. UV/VIS (MeOH): λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 234 (15 460), 261 (9030) and 354 (1010).

Bis[*N*,*N*,*N*′*N*′-tetrakis(2-pyridylmethyl)benzene-1,4-diamine]ruthenium(II) bis(hexafluorophosphate) [Ru(1,4-tpbd)$_2$][PF$_6$]$_2$·3H$_2$O. The compounds 1,4-tpbd (200 mg, 0.424 mmol) and [RuCl$_2$(C$_6$H$_5$CN)$_4$] (62 mg, 0.104 mmol) in ethanol (100 cm^3) were heated under reflux under argon for 48 h. The resulting yellow solution was evaporated to dryness and the residue redissolved in the minimum volume of water; 2 mol dm^{-3} NaOH was added dropwise until pH 9. The precipitated unchanged ligand was filtered off and the crude product precipitated by addition of a saturated aqueous solution of NH$_4$PF$_6$. Purification was achieved by column chromatography in silica gel using CH$_3$CN–saturated aqueous KNO$_3$–water (14 : 2 : 1). The main fraction containing [Ru(1,4-tpbd)$_2$]$^{2+}$ eluted in the last, yellow band. Yellow [Ru(1,4-tpbd)$_2$][PF$_6$]$_2$ was precipitated by addition of saturated aqueous NH$_4$PF$_6$ and recrystallized from water–acetonitrile (2 : 1). Yield 54 mg, 48% (Found: C, 51.72; H, 3.88; N, 11.93. $C_{60}H_{62}F_{12}N_{12}O_3RuP_2$ requires C, 51.84; H, 4.50; N, 12.09%). ^{1}H NMR (CD$_3$CN): δ 4.08 (d, 2 H, CH$_2$ co-ordinated, $J = 20.1$), 4.18 (d, 2 H, CH$_2$ co-ordinated, $J = 20.1$), 4.27 (d, 2 H, CH$_2$ co-ordinated, $J = 19.1$), 4.43 (d, 2 H, CH$_2$ co-ordinated, $J = 19.1$), 4.77 (s, 8 H, CH$_2$ unco-ordinated), 6.22 (m, 8 H, C$_6$H$_4$), 6.99–7.46 (m, 8 H, py H3 + H5 co-ordinated + un-coordinated), 7.70–7.94 (m, 8 H, py H4 co-ordinated + unco-ordinated), 8.24 (d, 2 H, py H6 co-ordinated, $J = 5.5$), 8.66 (d, 4 H, py H6 unco-ordinated, $J = 4.7$) and 9.19 (d, 2 H, py H6 co-ordinated, $J = 5.6$). ^{13}C NMR (CD$_3$CN): δ 57.88 (CH$_2$ unco-ordinated), 64.76, 71.91 (CH$_2$ co-ordinated), 112.84 (phenyl CH), 121.28, 122.93, 123.72, 123.95, 125.86, 126.60 (py C3 + C5 co-ordinated + unco-ordinated), 138.09, 138.66, 140.96 (py C4 co-ordinated + unco-ordinated), 139.30, 146.12 (phenyl C, co-ordinated + unco-ordinated), 149.40, 153.04, 156.13 (py C6 co-ordinated + unco-ordinated), 159.34 (py C2 unco-ordinated), 162.03, 165.88 (py C2 co-ordinated). UV/VIS (CH$_3$CN): λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 255 (52 100) and 389 (13 750).

Poly{[*N*,*N*,*N*′*N*′-tetrakis(2-pyridylmethylbenzene)-1,4-diamine]iron(II) chloride} [Fe(1,4-tpbd)]$_n$Cl$_{2n}$. This synthesis was carried out under argon using standard Schlenk techniques. Anhydrous FeCl$_2$ (32 mg, 0.26 mmol) in CH$_3$CN (5 cm^3) was added to a solution of 1,4-tpbd (120 mg, 0.26 mmol) in CH$_3$CN (25 cm^3) together with a few iron turnings. The stirred mixture was heated under reflux for 1 h, cooled and allowed to crystallize for 2 h and finally filtered under argon. The resulting yellow crystals were stable in air, yield 85 mg, 56% (Found: C, 60.90; H, 4.75; Cl, 11.63; N, 14.25. $C_{30}H_{28}Cl_2FeN_6$ requires C, 60.12; H, 4.71; Cl, 11.83; N, 14.02%). FAB mass spectrum: *m*/*z* 1035 {[FeCl(1,4-tpbd)$_2$]$^+$, 1}, 619 {[Fe$_2$Cl(1,4-tpbd)]$^+$, 20} and 563 {[FeCl(1,4-tpbd)]$^+$, 60%}.

Poly{[*N*,*N*,*N*′*N*′-tetrakis(2-pyridylmethylbenzene)-1,4-diamine]nickel(II) perchlorate}, [Ni(1,4-tpbd)]$_n$[ClO$_4$]$_{2n}$·nH$_2$O. The compound Ni(ClO$_4$)$_2$·6H$_2$O (38.7 mg, 0.106 mmol) in hot absolute ethanol (5 cm^3) was slowly added to a stirred solution of 1,4-tpbd (50 mg, 0.106 mmol) in hot absolute ethanol (10 cm^3). The product precipitated immediately as a green solid, which was filtered off using an extra fine filter, yield 62 mg, 80% (Found: C, 47.56; H, 4.12; Cl, 9.43; N, 11.47. $C_{30}H_{28}Cl_2N_6NiO_8$) requires C, 48.16; H, 4.04; Cl, 9.48; N, 11.23%). FAB mass spectrum: *m/z* 1101 {$[Ni(1,4\text{-tpbd})_2(ClO_4)]^+$, 30}, 1002 {$[Ni(1,4\text{-tpbd})_2]^+$, 25}, 887 {$[Ni_2(1,4\text{-tpbd})(ClO_4)_3]^+$, 28}, 788 {$[Ni_2(1,4\text{-tpbd})(ClO_4)_2]^+$, 27}, 629 {$[Ni(1,4\text{-tpbd})(ClO_4)]^+$, 75} and 530 {$[Ni(1,4\text{-tpbd})]^+$, 100%}.

X-Ray crystallography

Crystals suitable for X-ray diffraction studies were isolated directly from reaction mixtures. Details of structure determinations are listed in Table 1. Intensities were measured using a Huber four-circle diffractometer, at room temperature for $[Pd_2Cl_2(1,4\text{-tpbd})][PdCl_3(dmso)]_2$. At room temperature crystals of $[ZnCl_2(1,4\text{-tpbd})]$ decayed rapidly in the X-ray beam, and the crystal was therefore cooled to 120 K, by means of a Crystostream cooler,[6] which reduced the problem. Cell dimensions were determined from reflections measured at $\pm 2\theta$. Data were corrected for background, Lorentz-polarization effects, and absorption. The structures were determined using SIR 92[7] and from subsequent difference electron-density maps and were refined by the minimization of $\Sigma w(|F_o| - F_c|)^2$ using a modification of ORFLS.[8] Crystals of $[ZnCl_2(1,4\text{-tpbd})]$ were twinned on (001) so that reflections *hkl* with $l = 2$, 9 and 13 were partly overlapped and were rejected, those with $l = 0$, 11 were almost totally overlapped and could therefore be unscrambled, and the reflections of remaining layers were not overlapped and could be used unaltered. Non-hydrogen atoms were refined anisotropically; hydrogen atoms of the ligand were kept at calculated positions (C–H 0.95 Å) with isotropic displacement parameters 20% larger than the equivalent isotropic displacement parameters of the atoms to which they were attached. Atomic scattering factors and anomalous dispersion corrections (for Zn and Pd) were from ref. 9.

CCDC reference number 186/924.

See http://www.rsc.org/suppdata/dt/1998/1751/ for crystallographic files in .cif format.

Results and Discussion

Our investigations with the bis(tridentate) ligand 1,4-tpbd demonstrate that this ligand shows 'schizodentate' character; co-ordination to transition-metal ions *via* either one or both of the tridentate ends is possible in 1 : 1, 1 : 2 and 2 : 1 metal : ligand complexes.

A mononuclear complex

The reaction of 1,4-tpbd with an excess of $ZnCl_2$ in dmso results in pale pink crystals of $[ZnCl_2(1,4\text{-tpbd})]$. This slight colouration is probably due to the presence of a trace amount of oxidized ligand (the one-electron oxidized form of the ligand, 1,4-tpbd$^{\cdot +}$, is purple[3]). Preparations using other solvents gave products which precipitated much faster yielding white microcrystalline materials. The solubility properties of the neutral $[ZnCl_2(1,4\text{-tpbd})]$ might be the reason for the precipitation of a mono- rather than a di- or poly-zinc complex. Preparations with large excesses of zinc did not alter the outcome. However electronic grounds cannot be excluded; co-ordination of one end of the ligand may withdraw electron density from the other end with the result that once the first metal is bound it is more difficult to bind the second. The ^{1}H NMR spectrum of $[ZnCl_2(1,4\text{-tpbd})]$ was recorded in $(CD_3)_2SO$ in both the presence and absence of extra zinc chloride. In the absence of additional Zn^{II} the signals in the spectrum of $[ZnCl_2(1,4\text{-tpbd})]$ are broad indicating, not surprisingly, rapid ligand exchange on the NMR timescale. When 3 equivalents of zinc chloride were added to the solution the signals sharpened and indeed multiplets were observed for the signals due to the aromatic protons. A singlet at δ 4.64 due to the eight methylene protons indicates that they are chemically equivalent despite the crystal structure which shows that only one end of the ligand is co-ordinated. This result can be interpreted such that the complex is still labile in the presence of excess of zinc and/or dinuclear in solution. Insolubility in solvents appropriate for low-temperature NMR studies has prevented investigation of this issue.

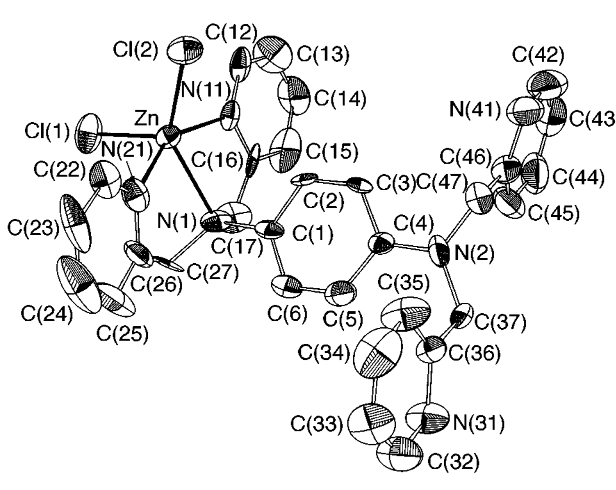


Fig. 1 An ORTEP[10] drawing of the cation in $Zn(1,4\text{-tpbd})Cl_2$

The crystal structure of neutral $[ZnCl_2(1,4\text{-tpbd})]$ is shown in Fig. 1. Selected distances and angles are listed in Table 2. The zinc atom is five-co-ordinated to three nitrogen atoms of the ligand and two chlorine atoms, with Zn–Cl(1) 2.277(4), Zn–Cl(2) 2.300(4), average Zn–N$_{py}$ 2.15(1) and Zn–N$_{amine}$ 2.26(1) Å. The co-ordination geometry is intermediate between that of a square pyramid and a trigonal bipyramid, but is closest to a tetragonal-pyramidal arrangement with Cl(1) at the apex. The sum of the C–N–C angles around the unco-ordinated phenylenediamine nitrogen, N(2), is 359.8° and C(4)–N(2) is only 1.37(1) Å. In contrast the sum of the C–N–C angles around the co-ordinated N(1) is 338.5° and C(1)–N(1) 1.49(1) Å. The planar geometry about the unco-ordinated amine nitrogen atom as well as the double-bond character for C(4)–N(2) indicates a π delocalization of this amine nitrogen atom lone pair with the aromatic system. A result of this delocalization is the quinoid character evident in the bond lengths of the aromatic linker.

A dinuclear complex

The reaction of 1,4-bpbd with $PdCl_4^{2-}$ in methanol–water yields the dinuclear palladium complex $[Pd_2Cl_2(1,4\text{-tpbd})]Cl_2$ as a relatively insoluble pale yellow microcrystalline material. However the cation of this complex could be structurally characterized in the orange crystalline compound $[Pd_2Cl_2(1,4\text{-tpbd})][PdCl_3(dmso)]_2$ which was obtained from the reaction of 1,4-tpbd with $PdCl_2$ in dmso. The cation and the anion in the structure of $[Pd_2Cl_2(1,4\text{-tpbd})][PdCl_3(dmso)]_2$ are shown in Fig. 2. An ORTEP diagram of the counter anion $[PdCl_3(dmso)]^-$ is shown since to our knowledge this is the first report of a crystal structure containing this particular anion, although there are several examples known for its platinum analogue.[11] Selected distances and angles for $[Pd_2Cl_2(1,4\text{-tpbd})][PdCl_3(dmso)]_2$ are listed in Table 3. In $[Pd_2Cl_2(1,4\text{-tpbd})]^{2+}$ the 1,4-tpbd bridges the two palladium atoms which are each co-ordinated to three nitrogen atoms and one chlorine atom in a square-planar arrangement with Pd–Cl 2.290(1), Pd–N$_{pyridyl}$ 2.009(3) and Pd–N$_{amine}$ 2.047(4) Å. Even though meridional co-ordination of this ligand might be expected to produce a more strained system these bond distances are shorter than the corresponding metal–donor bonds in $[ZnCl_2(1,4\text{-tpbd})]$. The cation has approximate *mm*2 symmetry with one mirror plane coincident

Table 1 Crystallographic data and experimental details*

	$[Pd_2Cl_2(1,4\text{-tpbd})][PdCl_3(dmso)]_2\cdot0.5H_2O$	$[ZnCl_2(1,4\text{-tpbd})]$
Formula	$C_{34}H_{41}Cl_8N_6O_{2.5}Pd_4S_2$	$C_{30}H_{28}Cl_2N_6Zn$
M	1347.62	608.88
Space group	$P2_1/n$	$P2_1$
a/Å	8.822(1)	8.369(2)
b/Å	36.340(5)	13.448(3)
c/Å	14.125(1)	13.330(4)
β/°	92.086(6)	111.19(1)
U/Å³	4525(1)	1399(1)
Z	4	2
T/K	294	120
D_c/g cm⁻³	1.978	1.446
F(000)	2637.20	628
Colour	Orange	Pale pink
Crystal shape	Lath	Tabular
Crystal size/mm	0.50 × 0.15 × 0.03	0.45 × 0.40 × 0.16
μ(Mo-Kα)/mm⁻¹	2.170	1.100
Absorption correction	Empirical	Integration
Transmission factors	0.705–1.210	0.727–0.851
Data collection range/°	$2 < 2\theta < 50$; $\pm h, +k, +l$	$3 < 2\theta < 55$; $\pm h, +k, +l$
No. reflections measured	8892	5288
R_{int}	0.032	0.170
No. unique reflections	7996	3352
No. observed reflections	5575 $[I > 3\sigma(I)]$	1976 $[I > 2\sigma(I)]$
No. variables	515	352
R	0.036	0.065
R'	0.046	0.073
Goodness of fit	1.094	1.395
$(\Delta/\sigma)_{max}$	0.035	0.028
ρ_{min}, ρ_{max}/e Å⁻³	−0.8(1), 0.7(1)	−1.1(1), 1.2(1)

* Details in common: monoclinic; 30 reflections centred; graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å); 0% decay of standards; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w^2(|F_o| - |F_c|)^2/\Sigma w^2(|F_o|)^2]^{\frac{1}{2}}$, $w = 1/\{[\sigma_{CS}(F^2) + 1.03F^2]^{\frac{1}{2}} - |F|\}$.

Table 2 Selected bond distances (Å) and angles (°) of $[ZnCl_2(tpbd)]$

Zn–Cl(1)	2.277(4)	C(1)–C(2)	1.411(15)
Zn–Cl(2)	2.300(4)	C(2)–C(3)	1.397(15)
Zn–N(21)	2.115(11)	C(3)–C(4)	1.401(15)
Zn–N(11)	2.178(9)	C(4)–N(2)	1.372(14)
Zn–N(1)	2.261(10)	C(4)–C(5)	1.424(18)
N(1)–C(17)	1.466(16)	C(5)–C(6)	1.386(18)
N(1)–C(1)	1.488(14)	N(2)–C(47)	1.416(19)
N(1)–C(27)	1.489(16)	N(2)–C(37)	1.442(17)
C(1)–C(6)	1.386(16)		
N(11)–Zn–N(21)	150.9(4)	Zn–N(1)–C(27)	99.9(8)
N(1)–Zn–N(21)	75.4(4)	C(2)–C(1)–C(6)	119.6(11)
Cl(1)–Zn–N(21)	99.7(3)	N(1)–C(1)–C(6)	121.7(11)
Cl(2)–Zn–N(21)	98.1(3)	N(1)–C(1)–C(2)	118.6(10)
N(1)–Zn–N(11)	76.5(4)	C(1)–C(2)–C(3)	120.4(10)
Cl(1)–Zn–N(11)	97.1(3)	C(2)–C(3)–C(4)	121.2(9)
Cl(2)–Zn–N(11)	96.1(3)	C(3)–C(4)–N(2)	121.8(11)
Cl(1)–Zn–N(1)	109.9(3)	C(5)–C(4)–N(2)	121.7(11)
Cl(2)–Zn–N(1)	135.3(3)	C(3)–C(4)–C(5)	116.4(10)
Cl(1)–Zn–Cl(2)	114.8(2)	C(4)–C(5)–C(6)	122.9(11)
C(1)–N(1)–C(17)	111.5(10)	C(1)–C(6)–C(5)	119.2(11)
C(17)–N(1)–C(27)	113.7(11)	C(4)–N(2)–C(47)	120.3(12)
Zn–N(1)–C(17)	105.7(8)	C(4)–N(2)–C(37)	118.6(11)
C(1)–N(1)–C(27)	113.3(11)	C(37)–N(2)–C(47)	120.8(11)
Zn–N(1)–C(1)	112.0(7)		

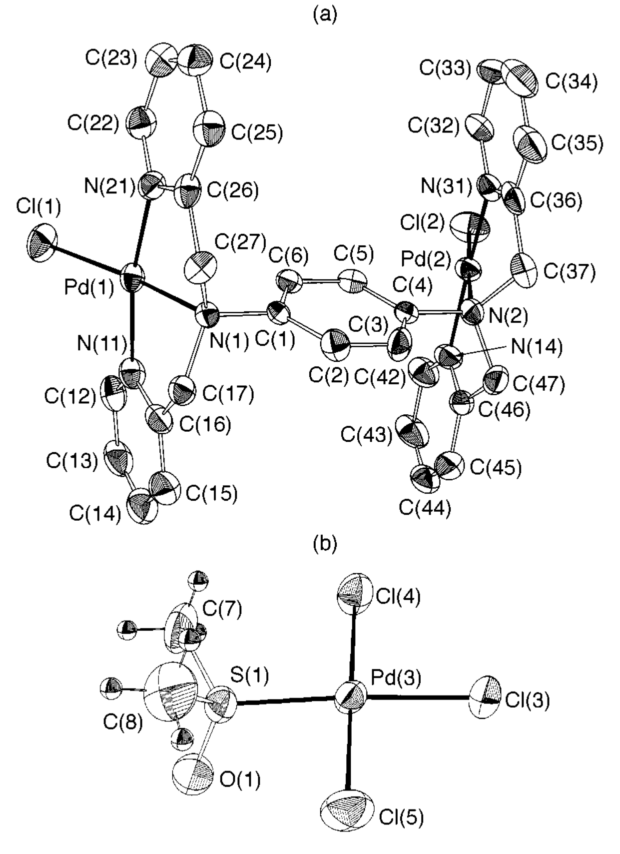


Fig. 2 An ORTEP[10] drawing of the cation (a) and the anion (b) in $[Pd_2Cl_2(1,4\text{-tpbd})][PdCl_3(dmso)]_2$

with the plane of the phenyl ring, and the other perpendicular to it and bisecting C(2)–C(3) and C(5)–C(6). The geometry of the palladium ion in the anion is square planar with Pd–Cl 2.300(1) and Pd–S 2.250(1) Å. There is a partially occupied water site. Again conjugation of the amine-based electrons with those of the linking benzene ring is reflected by a quinoid character for the bond distances of the phenylenediamine moiety and the planar geometry of the amine nitrogen atoms. The 'bite' angles of the tridentate ends of 1,4-tpbd in $[Pd_2Cl_2(1,4\text{-tpbd})]^{2+}$ are very similar to those measured for the related terpy complex $[PdCl(terpy)]^+$. The N–Pd–N angles reported for the distorted $[PdCl(terpy)]^+$ cation are 79 and 82°,[12] similar to those for $[Pd_2Cl_2(1,4\text{-tpbd})]^{2+}$ of 83°. The similarities between these structures also support the less aliphatic nature of the tertiary amine donor in 1,4-tpbd.

In the structures of the di- and tetra-positive cations $[Pd_2Cl_2(1,4\text{-tpbd})]^{2+}$ (Fig. 2) and $[Cu_2(1,4\text{-tpbd})(H_2O)_4]^{4+}$ [3] the

Table 3 Selected bond distances (Å) and angles (°) of $[Pd_2Cl_2(tpbd)][PdCl_3(dmso)]_2$

Cation			
Pd(1)–N(11)	2.005(5)	N(1)–C(27)	1.508(8)
Pd(1)–N(21)	2.004(5)	N(2)–C(4)	1.480(7)
Pd(1)–N(1)	2.051(5)	N(2)–C(37)	1.503(9)
Pd(1)–Cl(1)	2.294(2)	N(2)–C(47)	1.504(8)
Pd(2)–N(31)	2.011(5)	C(1)–C(2)	1.399(8)
Pd(2)–N(41)	2.016(5)	C(1)–C(6)	1.376(8)
Pd(2)–N(2)	2.042(5)	C(2)–C(3)	1.378(9)
Pd(2)–Cl(2)	2.286(2)	C(3)–C(4)	1.374(9)
N(1)–C(1)	1.480(7)	C(4)–C(5)	1.383(8)
N(1)–C(17)	1.511(8)	C(5)–C(6)	1.395(8)
N(11)–Pd(1)–N(21)	166.4(2)	C(17)–N(1)–C(27)	112.2(5)
N(1)–Pd(1)–N(21)	83.2(2)	C(4)–N(2)–C(37)	111.4(5)
Cl(1)–Pd(1)–N(21)	97.1(1)	C(4)–N(2)–C(47)	111.9(5)
N(1)–Pd(1)–N(11)	83.3(2)	C(37)–N(2)–C(47)	112.4(5)
Cl(1)–Pd(1)–N(11)	96.5(1)	C(2)–C(1)–C(6)	119.6(5)
Cl(1)–Pd(1)–N(1)	171.8(1)	N(1)–C(1)–C(6)	121.2(5)
N(31)–Pd(2)–N(41)	167.1(2)	N(1)–C(1)–C(2)	119.2(5)
N(2)–Pd(2)–N(31)	83.3(2)	C(1)–C(2)–C(3)	119.5(6)
Cl(2)–Pd(2)–N(31)	96.7(2)	C(2)–C(3)–C(4)	121.0(6)
N(2)–Pd(2)–N(41)	83.8(2)	C(3)–C(4)–C(5)	119.7(5)
Cl(2)–Pd(2)–N(41)	96.2(2)	N(2)–C(4)–C(3)	120.0(5)
Cl(2)–Pd(2)–N(2)	177.0(2)	N(2)–C(4)–C(5)	120.3(5)
C(1)–N(1)–C(17)	111.6(4)	C(4)–C(5)–C(6)	119.9(5)
C(1)–N(1)–C(27)	112.3(5)	C(1)–C(6)–C(5)	120.2(5)
Anion			
Pd(3)–S(1)	2.245(2)	Pd(4)–Cl(8)	2.283(2)
Pd(3)–Cl(3)	2.311(2)	S(1)–O(1)	1.467(5)
Pd(3)–Cl(4)	2.284(2)	S(1)–C(7)	1.759(9)
Pd(3)–Cl(5)	2.296(2)	S(1)–C(8)	1.757(8)
Pd(4)–S(2)	2.256(2)	S(2)–O(2)	1.470(6)
Pd(4)–Cl(6)	2.312(2)	S(2)–C(9)	1.763(8)
Pd(4)–Cl(7)	2.312(2)	S(2)–C(10)	1.770(9)
Cl(4)–Pd(3)–S(1)	94.01(7)	Pd(3)–S(1)–O(1)	114.9(2)
Cl(5)–Pd(3)–S(1)	86.79(8)	Pd(3)–S(1)–C(7)	114.4(3)
Cl(3)–Pd(3)–S(1)	176.66(6)	Pd(3)–S(1)–C(8)	109.3(4)
Cl(4)–Pd(3)–Cl(5)	177.13(9)	Pd(4)–S(2)–O(2)	113.9(3)
Cl(3)–Pd(3)–Cl(4)	88.01(8)	Pd(4)–S(2)–C(9)	114.5(4)
Cl(3)–Pd(3)–Cl(5)	91.32(8)	Pd(4)–S(2)–C(10)	111.3(3)
Cl(8)–Pd(4)–S(2)	90.8(1)	O(1)–S(1)–C(8)	109.7(5)
Cl(7)–Pd(4)–S(2)	88.89(8)	O(1)–S(1)–C(7)	107.5(4)
Cl(6)–Pd(4)–S(2)	178.02(9)	C(7)–S(1)–C(8)	100.1(5)
Cl(7)–Pd(4)–Cl(8)	172.44(9)	O(2)–S(2)–C(9)	107.7(4)
Cl(6)–Pd(4)–Cl(8)	90.3(1)	O(2)–S(2)–C(10)	108.8(5)
Cl(6)–Pd(4)–Cl(7)	90.15(8)	C(9)–S(2)–C(10)	99.5(5)

donor nitrogen atoms and the metal atom to which they are co-ordinated are almost coplanar with the consequence of a *trans* arrangement of two pyridine groups at each metal ion. This *pseudo*-meridional co-ordination is expected in the case of the palladium complex, given the preference of palladium for square planar geometry. It is, however, a unusual arrangement for the bis(2-pyridylmethyl)amine ends of the ligand. The fact that a similar arrangement is present in the copper complex points towards the fact that a meridional-type arrangement may be preferred by the ligand. In contrast, the structures of complexes of bis(picolyl)amine and its N-substituted derivatives show almost exclusively facial co-ordination.[13]

A bis-coordinated complex

The mononuclear bis-co-ordinated complex $[Ru(1,4\text{-tpbd})_2][PF_6]_2$ was prepared from the reaction of 1,4-tpbd and $[RuCl_2(C_6H_5CN)_4]$ in 1 : 4 proportions in ethanol. The elemental analysis, mass and NMR spectra confirm the formulation. The presence of both co-ordinated and unco-ordinated picolyl groups is clearly evident in the NMR spectra of $[Ru(1,4\text{-tpbd})_2][PF_6]_2$. The ^1H NMR spectrum is shown in Fig. 3. The four methylene protons of the unco-ordinated end of the ligand are equivalent and appear as a singlet at δ 4.77. The methylene protons of the co-ordinated end are constrained and show geminal coupling patterns. The four doublets due to these protons are shifted slightly upfield. The signals for the α-pyridine protons are split in a corresponding fashion. The α-protons of the unco-ordinated pyridines are seen as a doublet at δ 8.66, whereas the α-protons of the co-ordinated pyridines are assigned to two doublets at δ 8.24 and 9.19. From the NMR results it is impossible to determine the co-ordination geometry of the tridentate ends of the ligand in $[Ru(tpbd)_2]^{2+}$, *i.e.* the ligand might be co-ordinated in either a *cis*- or *trans*-facial or in a meridional fashion. The apparent trigonal geometry around the amine nitrogen atoms in the structures of the complexes of Zn, Pd and Cu[3] suggest a preference for the tridentate end of the ligand for meridional co-ordination. However one indirect piece of evidence we have to support a possible facial co-ordination of the tridentate ends of the two 1,4-tpbd ligands in $[Ru(1,4\text{-tpbd})_2]^{2+}$ is the crystal structure of a mononuclear ruthenium(II) complex of a related phenyl-substituted bis(picolyl)amine ligand, $[Ru(bpba)_2][PF_6]_2$ [bpba = *N*,*N*-bis-(2-pyridylmethyl)aniline] which shows *cis*-facial ligand co-ordination.[14] The ^1H NMR signals arising from the aromatic and aliphatic protons of the co-ordinated end of $[Ru(tpbd)_2]^{2+}$ show similar patterns to those assigned to the corresponding protons of bpba in the ^1H NMR spectrum of $[Ru(bpba)_2]^{2+}$,[14] supporting the assignment of similar *cis*-facial co-ordination geometries.

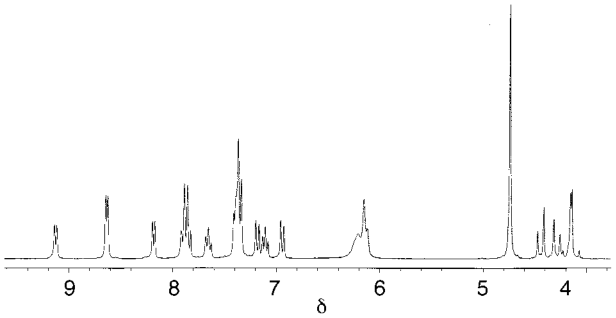


Fig. 3 Proton spectrum of $[Ru(1,4\text{-tpbd})_2][PF_6]_2$

The cyclic voltammogram of $[Ru(1,4\text{-tpbd})_2][PF_6]_2$ shows one reversible wave centered at 1.196 V. This is assigned to a Ru^{II}–Ru^{III} redox process rather than ligand oxidation. Thus ligand oxidation is suppressed upon co-ordination to ruthenium. (A reversible oxidation at 310 mV and an irreversible oxidation at 670 mV is observed for free 1,4-tpbd.[3])

Polynuclear complexes/co-ordination polymers

The evidence so far suggests that polymeric or oligomeric nickel(II) and iron(II) complexes have been prepared, however in the absence of crystal structures we have found it difficult unambiguously to characterize these materials. The relatively insoluble products obtained from the reaction of 1,4-tpbd with nickel(II) and iron(II) salts are microcrystalline, however crystals suitable for X-ray crystallography have so far eluded us. Elemental analyses are consistent with polymeric formulations. The pattern of the pyridine absorptions around 1600 cm^{-1} in the IR spectra of $[Fe(1,4\text{-tpbd})]_nCl_{2n}$ and $[Ni(1,4\text{-tpbd})]_n[ClO_4]_{2n}$ indicate co-ordination of all the pyridine groups since they bear greater resemblance to the spectra obtained for the complexes which show co-ordination of both tridentate ends of the ligand, *i.e.* the dinuclear 1,4-tpbd-bridged palladium(II) and copper(II) complexes, compared to those of the monoco-ordinated zinc(II) and bis[ruthenium(II)]-complex.

Mass spectrometry (FAB) supports the assignment of polymeric formulations. The spectra of $[Fe(1,4\text{-tpbd})]_nCl_{2n}$ and

$[Ni(1,4\text{-tpbd})]_n[ClO_4]_{2n}$ show several peaks consistent with the mass of the ions expected from decomposition of a polymer, *e.g.* peaks can be assigned to ions of the composition 1 : 2 metal : ligand and 2 : 1 metal : ligand ratios. In contrast and as expected, peaks assignable to 2 : 1 metal : ligand combinations are observed while peaks for 1 : 2 metal : ligand combinations are absent in the mass spectra of the crystallographically characterized dinuclear complexes $[Pd_2(1,4\text{-tpbd})Cl_2][Pd(dmso)Cl_3]_2$ and $[Cu_2(1,4\text{-tpbd})(H_2O)_4][S_2O_6]_2$.

An effective magnetic moment of *ca.* 6 μ_B ($\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}) per iron(II) at room temperature was obtained for $[Fe(1,4\text{-tpbd})]_nCl_{2n}$ at room temperature. The Mössbauer spectrum at room temperature shows a doublet with an isomer shift, δ, of 0.803(2) mm s^{-1} and a quadrupole splitting, ΔE_Q, of 2.963(4) mm s^{-1}. These results are consistent for high-spin iron(II).

If co-ordination polymers with 1,4-tpbd, tppz and dpqtpy are eventually structurally characterized they are expected to show quite different topologies: the structures of the dinuclear complexes $[Pd_2Cl_2(1,4\text{-tpbd})]^{2+}$ and $[Cu_2(1,4\text{-tpbd})(H_2O)_4]^{4+}$ reveal that the ligand exists in two different conformations. This is reflected in the steric arrangement of the two ends; the metal planes in the dipalladium complex are located on the same side of the benzene linker, whilst a *trans* arrangement is evident in the case of the dicopper complex. The cause of these '*cis*' and '*trans*' arrangements is probably due simply to crystal-packing effects. However the consequence of these conformations in oligomeric systems will be a puckering of the linear molecules. In the case of dpqtpy, a one-dimensional polymer is expected to be rod-like; only rotation about the interannular C–C bond linking the terpy-based ends is feasible. The ligand tppz is even less flexible, although it was shown to be highly twisted in the structures reported for the dinuclear copper and decanuclear zinc complex.[4]

Conclusion

The isolation of a mononuclear complex $[ZnCl_2(1,4\text{-tpbd})]$, and a bis complex, $[Ru(1,4\text{-tpbd})_2][PF_6]_2$, of 1,4-tpbd opens up fascinating possibilities, for example the co-ordination of a second and different metal by the non-co-ordinated tridentate ends. Co-ordination of a second ligand to starting materials like the dinuclear $[Pd_2Cl_2(1,4\text{-tpbd})]^{2+}$ and $[Cu_2(1,4\text{-tpbd})(H_2O)_4]^{4+}$[3] may lead to similar species. In fact these complexes represent well characterized examples of the types of building blocks needed to carry out the 'complexes-as-metals, complexes-as-ligands' approach to the assembly of oligomers proposed by Constable and Balzani and co-workers.[15] Future work will include the reaction of $[ZnCl_2(1,4\text{-tpbd})]$ and $[Ru(1,4\text{-tpbd})_2][PF_6]_2$ with a second transition-metal ion to give heterodinuclear complexes of the type $[L_nM(1,4\text{-tpbd})ZnCl_2]^{n+}$, $[L_nM(1,4\text{-tpbd})Ru(1,4\text{-tpbd})]^{n+}$ or heterotrinuclear complexes of the type $[L_nM(1,4\text{-tpbd})Ru(1,4\text{-tpbd})ML_n]^{n+}$. In summary, we have now characterized transition-metal complexes with M : 1,4-tpbd ratios of 1 : 1, 2 : 1 and 1 : 2. Using combinations of these units the strategic build-up of linear heteronuclear complexes can be envisioned.

Acknowledgements

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References

1 F. Vögtle, *Supramolecular Chemistry*, Wiley, Chichester, 1991; *Supramolecular Chemistry*, eds. V. Balzani and L. De Cola, Kluwer, Dordrecht, 1992; *Transition Metals in Supramolecular Chemistry*, eds. L. Fabrizzi and A. Poggi, Kluwer, Dordrecht, 1994.

2 B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1989, **111**, 5962; B. F. Abrahams, M. J. Hardie, B. F. Hoskins, R. Robson and G. A. Williams, *J. Am. Chem. Soc.*, 1992, **114**, 10 641; K. T. Potts, K. A. G. Raiford and M. Keshavarz-K, *J. Am. Chem. Soc.*, 1993, **115**, 2793; M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151; S. Kawata, S. Kitagawa, M. Kondo, I. Furuchi and M. Munakata, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 1759; S. Descurtins, H. W. Schmalle, P. Schneuwly, L. Zheng, J. Ensling and A. Hauser, *Inorg. Chem.*, 1995, **34**, 5501; M. Ohba, H. Okawa, T. Ito and A. Ohto, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 1545; M. Ohba, N. Maruono, H. Okawa, T. Enoki and J.-M. Latour, *J. Am. Chem. Soc.*, 1994, **116**, 1545; G. D. Munno, R. Ruiz, F. Lloret, J. Faus, R. Sessoli and M. Julve, *Inorg. Chem.*, 1995, **34**,408; L. Carluccia, G. Ciani, D. M. Proserpio and A. Sironi, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 1895; H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo and C. Floriani, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 1446; C. Bowes and G. A. Ozin, *Adv. Mater.*, 1996, **8**, 13 and refs. therein.

3 T. Buchen, A. Hazell, L. Jessen, C. J. McKenzie, L. Preuss Nielsen, J. Z. Pedersen and D. Schollmeyer, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 2697.

4 M. Graf, B. Greaves and H. Stoeckli-Evans, *Inorg. Chim. Acta*, 1993, **204**, 239; M. Graf and H. Stoeckli-Evans, *Acta Crystallogr.*, *Sect. C*, 1994, **50**, 1461.

5 E. C. Constable, A. M. W. Cargill Thompson and S. Greulich, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 1444; E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 1615; *New J. Chem.*, 1992, **16**, 855; *J. Chem. Soc.*, *Dalton Trans.*, 1992, 3467; E. C. Constable, *Prog. Inorg. Chem.*, 1994, **42**, 67; M. T. Indelli, F. Scandola, J.-P. Collin, J.-P. Sauvage and A. Sour, *Inorg. Chem.*, 1996, **35**, 303.

6 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.

7 A. Altomare, B. Cascarano, C. Giacovazzo, A. Guagliardi, A. M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.

8 W. T. Busing, K. O. Martin and H. A. Levy, ORFLS, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, TN, 1962.

9 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, p. 72.

10 M. N. Burnett and C. K. Johnson, ORTEP III, Report ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN, 1996.

11 R. Melanson, J. Hubert and F. D. Rochon, *Acta Crystallogr.*, *Sect. B*, 1976, **32**, 1914; N. Veldman and A. L. Spek, *Acta Crystallogr.*, *Sect. C*, 1994, **32**, 1572; P. P. Khodadad and N. Rodier, *Acta Crystallogr.*, *Sect. C*, 1987, **43**, 1690; P. B. Viossat, P. Toffoli, P. P. Khodadad and N. Rodier, *Acta Crystallogr.*, *Sect. C*, 1988, **44**, 92.

12 G. M. Intille, C. E. Pfluger and W. A. Baker, jun., *J. Cryst. Mol. Struct.*, 1973, **3**, 47.

13 S. Larsen, K. Michelsen and E. Pedersen, *Acta Chem. Scand.*, *Sect. A*, 1986, **40**, 63; J. Glerup, P. A. Goodson, D. J. Hodgson, K. Michelsen, K. M. Nielsen and H. Wiehe, *Inorg. Chem.*, 1992, **31**, 4611; R. J. Butcher and A. W. Addison, *Inorg. Chim. Acta*, 1989, **158**, 211; S. Pal, M. K. Chan and W. H. Armstrong, *J. Am. Chem. Soc.*, 1992, **114**, 6398; S. Pal, M. M. Olmstead and W. H. Armstrong, *Inorg. Chem.*, 1995, **34**, 4708; M. Palaniandavar, T. Pandiyan, M. Laksminarayanan and H. Manohar, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 455; A. Hazell, K. B. Jensen, C. J. McKenzie, O. Simonsen and H. Toftlund, *Inorg. Chim. Acta*, 1997, **257**, 163.

14 A. Hazell, C. J. McKenzie and L. Preuss Nielsen, unpublished work.

15 G. Denti, S. Serroni, S. Campagna, A. Junis, M. Ciano and V. Balzani, in *Perspectives in Coordination Chemistry*, eds. A. F. Williams, C. Floriani and A. E. Merbach, VCH, Basel, 1992, p. 153; E. C. Constable, in *Transition Metals in Supramolecular Chemistry*, eds. L. Fabbrizzi and A. Poggi, NATO ASI Series, 1994, p. 81.

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