Dimorphs of [1,2-Bis(diphenylphosphino)ethane]dichloronickel(II)†

Richard Busby, Michael B. Hursthouse, Penelope S. Jarrett,* Christian W. Lehmann, K. M. Abdul Malik and Coral Phillips
School of Chemistry and Applied Chemistry, University of Wales College of Cardiff, P.O. Box 912, Cardiff CF1 3TB, UK

The two known forms, **A** and **B**, of [1,2-bis(diphenylphosphino)ethane]dichloronickel(II), [Ni(dppe)Cl$_2$], were synthesised and identified by IR spectroscopy. The spectra showed that form **A** had a lower symmetry than form **B**. The forms were also found to differ by solid-state ^{31}P NMR spectroscopy and powder X-ray diffraction, but the solution properties were identical. The IR spectrum of the dichloromethane solvate of [Ni(dppe)Cl$_2$] was the same as that of form **B** but with a strong additional band due to CH$_2$Cl$_2$. The X-ray diffraction pattern from this sample matched that calculated for a previously published crystal structure of [Ni(dppe)Cl$_2$]·CH$_2$Cl$_2$, thus identifying the form used in that work. Crystals of form **A** obtained from acetone were used for a single-crystal X-ray structure determination. Comparison of the molecular structures showed that both forms have the same chelate-ring conformation (δ) but differ in the orientations of the phenyl rings. There is a non-crystallographic two-fold axis in form **B** which is absent from **A**, explaining the additional bands present in the IR spectrum of the latter. Solid-state ^{31}P NMR was better than IR spectroscopy at distinguishing the two forms from each other and from mixtures.

Nickel(II) bis(phosphine) complexes continue to be of interest, both as catalysts[1] and for their relationship to complexes with anticancer activity.[2] Two forms of the compound [Ni(dppe)Cl$_2$] [dppe = 1,2-bis(diphenylphosphino)ethane] were first distinguished using IR spectroscopy by Nakamoto and co-workers,[3] who labelled them **A** and **B**. The spectrum of form **A** showed more bands than form **B**, and the spectrum of the latter was similar to those of [Ni(dppe)Br$_2$] and [Ni(dppe)I$_2$]. All the compounds were obtained from alcoholic solutions. However, when a crystal structure of [Ni(dppe)Cl$_2$]·CH$_2$Cl$_2$ was published[4] no indication was given as to whether it was the solvate of form **A**, form **B** or some entirely new form. We have therefore synthesised and studied by several techniques both of the forms described by Nakamoto and co-workers[3] in order to discover (*i*) which (if either) corresponded to the published crystal structure and (*ii*) the nature of the difference between the two forms.

Experimental

Syntheses.—These were performed using a number of solvents and solvent mixtures and a variety of concentrations. The syntheses of the samples used for the crystallography and powder diffraction are given.

Form **A**. A suspension of dppe (Strem Chemicals; 0.841 g, 2.11 mmol) in hot propan-2-ol (50 cm^3) was added to a solution of NiCl$_2$·6H$_2$O (0.502 g, 2.11 mmol) in hot propan-2-ol–methanol (2 : 1, 20 cm^3), which turned orange. The mixture was stirred (30 min) and an orange powder collected by filtration (crude yield > 75%) (Found: C, 59.3; H, 4.7. Calc. for C$_{26}$H$_{24}$Cl$_2$NiP$_2$: C, 59.1; H, 4.6%). Recrystallisation from hot acetone yielded a sample suitable for crystallography.

Form **B**. A solution of dppe (2.00 g, 5.04 mmol) in CH$_2$Cl$_2$ (25 cm^3) was added dropwise to a solution of NiCl$_2$·6H$_2$O (1.19 g, 5.01 mmol) in ethanol (20 cm^3), which became dark red. The mixture was stirred (30 min) and the dark orange crystals were collected by filtration, washed with diethyl ether (crude yield 2.44 g, 92%) and recrystallised from dichloromethane–ethanol (1 : 1, v/v) (Found: C, 53.5; H, 4.3. Calc. for C$_{28}$H$_{26}$Cl$_4$NiP$_2$: C, 52.9; H, 4.3%. Without CH$_2$Cl$_2$, prepared in EtOH, Found: C, 59.4; H, 4.6. Calc. for C$_{26}$H$_{24}$Cl$_2$NiP$_2$: C, 59.1; H, 4.6%).

Physical Measurements.—Microanalyses were performed on a Perkin Elmer 240B autoanalyser. UV/VIS spectra were recorded on a Pye-Unicam SP800 UV spectrophotometer or on a Phillips PU 8700 series UV/VIS spectrophotometer and magnetic susceptibilities were measured on a magnetic susceptibility balance from Sherwood Scientific. IR spectra were recorded on a Perkin Elmer 733 infrared spectrometer, a Perkin Elmer 577 infrared spectrometer, a Perkin Elmer 1600 series FTIR spectrometer or a Pye-Unicam SP3-200 infrared spectrophotometer as Nujol mulls between KBr or CsI plates. The ^{31}P-{H} NMR solution spectra were obtained on a JEOL FX90Q spectrometer operating at 36.23 MHz and the solid-state ^{31}P NMR spectra on a Bruker MSL-300 at 121.5 MHz with high-power proton decoupling, cross polarisation from protons and magic angle spinning (CPMAS) or by the SERC solid-state NMR service at Durham on a Varian VXR 300 operating at 121.4 MHz as single-pulse spectra with proton decoupling and magic angle spinning (SPMAS). Spin rates were 4.7–4.8 kHz and the reference was external H$_3$PO$_4$. For the CPMAS determination, contact times were 1 ms, pulse-cycle repetition times were 10–30 s and receiver dead times 15 μs. For the SPMAS determination the relaxation delay was 60 s. Mass spectra were acquired by the SERC mass spectrometry centre in Swansea using a VG Masslab model 12-253 quadrupole mass spectrometer in ACE (alternate scan electron impact and ammonia chemical ionisation) mode. X-Ray powder diffraction data were collected on a Philips PW1050 diffractometer controlled by a BBC microcomputer *via* a PW1710 interface using Cu-Kα radiation with a nickel filter. The goniometer had symmetrical reflection geometry (*i.e.* it uses parafocussing). The step size was 0.025° in 2θ with a collection time of 3 s per point. Theoretical powder diffraction patterns were generated using the Lazy-Pulverix[5] program MS-DOS Version 1.1.0 running on the Convex computer at the SERC Daresbury Laboratory.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Crystallographic data for [Ni(dppe)Cl_2] (form **A**)

Formula	$C_{26}H_{24}Cl_2NiP_2$
M	528.02
Space group	$P2_1/c$
a/Å	11.443(1)
b/Å	13.384(2)
c/Å	15.994(11)
β/°	99.04
U/Å^3	2419.10
D_c/g cm^{-3}	1.450
Z	4
F(000)	1088
μ(calc.)/cm^{-1}	11.70
θ Range for cell/°	2.5–25
θ Range for data/°	2.36–28.12
No. of data collected	4006
No. of data used [$F_o > 3\sigma(F_o)$]	1560
R, R'*	0.0342, 0.0369

* $R = \Sigma||F_o - F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, unit weights.

Table 2 Fractional atomic coordinates (× 10^4) for [Ni(dppe)Cl_2] (form **A**)

Atom	x	y	z
Ni	1266(1)	2196(1)	2065(1)
Cl(1)	115(2)	2658(2)	2971(1)
Cl(2)	2854(2)	2031(2)	3030(1)
P(1)	−267(2)	2113(2)	1095(1)
P(2)	2309(2)	1824(2)	1099(1)
C(1)	156(7)	1414(6)	206(4)
C(2)	1346(7)	1816(6)	60(4)
C(112)	−1386(5)	3355(4)	−185(3)
C(113)	−1856(5)	4262(4)	−510(3)
C(114)	−1766(5)	5110(4)	3(3)
C(115)	−1206(5)	5051(4)	842(3)
C(116)	−736(5)	4143(4)	1167(3)
C(111)	−827(5)	3295(4)	654(3)
C(122)	−2590(5)	1888(3)	1429(3)
C(123)	−3515(5)	1342(3)	1678(3)
C(124)	−3352(5)	337(3)	1898(3)
C(125)	−2265(5)	−122(3)	1868(3)
C(126)	−1340(5)	425(3)	1618(3)
C(121)	−1503(5)	1430(3)	1399(3)
C(212)	4054(5)	3280(4)	1580(2)
C(213)	4952(5)	3930(4)	1430(2)
C(214)	5319(5)	3946(4)	639(2)
C(215)	4788(5)	3312(4)	−3(2)
C(216)	3891(5)	2662(4)	146(2)
C(211)	3524(5)	2646(4)	938(2)
C(222)	2360(4)	−97(4)	1768(3)
C(223)	2672(4)	−1105(4)	1813(3)
C(224)	3433(4)	−1485(4)	1290(3)
C(225)	3883(4)	−856(4)	722(3)
C(226)	3572(4)	152(4)	677(3)
C(221)	2810(4)	532(4)	1200(3)

X-Ray Crystallography.—Orange-brown crystals of form **A** of [Ni(dppe)Cl_2] were grown from acetone. A half-hexagonal crystal (0.27 × 0.22 × 0.03 mm) was mounted on a glass fibre and X-ray diffraction data collected on an Enraf-Nonius FAST-TV area-detector system utilising Mo-Kα radiation (λ = 0.710 69 Å) from an FR571 rotating-anode generator operating at 2.75 kW.[6] The reflection intensities from one hemisphere were merged to form a unique dataset (R_{int} = 0.052). The structure was solved by the Patterson method and further developed by the Fourier difference method with full least-squares refinement using SHELX 76.[7] The hydrogen atoms and carbons of the phenyl rings were fixed with idealised geometry. All non-hydrogen atoms were refined anisotropically.

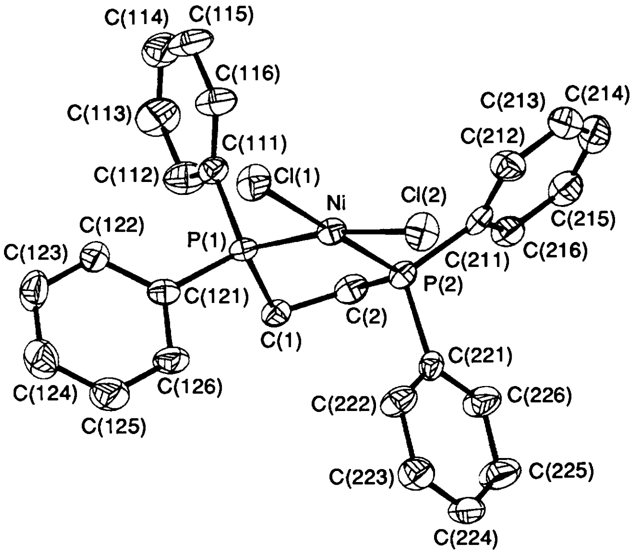

Fig. 1 Molecular structure of form **A** of [Ni(dppe)Cl_2] with the atomic numbering scheme

An empirical absorption correction was applied using DIFABS.[8] CHEM-X[9] was used to display the crystallographic results and produce Figs. 2 and 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results

The assertion by Nakamoto and co-workers[3] that form **A** can be obtained from ethanol or methanol (the method of Hudson *et al.*[10]) and form **B** from a 2:1 molar mixture of propan-2-ol and methanol (the method of van Hecke and Horrocks[11]) now appears too simple. From ethanol we obtained form **A** when the $NiCl_2 \cdot 6H_2O$ solution was added to the dppe solution. If the order of the addition was reversed, then form **A** resulted from more dilute preparations (3.6 or 8.6 μmol dm^{-3} in Ni^{II}) and form **B** from concentrated ones (> 24 μmol dm^{-3} in Ni^{II}). The preparation in propan-2-ol and methanol gave form **A** in some hands and form **B** in others, with no obvious relation to the order of addition or concentration. Recrystallisation of form **A** from acetone gave form **A**. Recrystallisation of either form from dichloromethane or dichloromethane–ethanol gave form **B** every time, with a molecule of CH_2Cl_2 incorporated. This was evident from the elemental analysis, and the C–Cl stretch was visible at 730 cm^{-1} in the IR spectrum.

Infrared spectra were used to distinguish the two forms initially, though this technique did not prove wholly reliable in some respects (see below). Nakamoto and co-workers[3] listed absorptions between 400 and 200 cm^{-1} for isotopically pure samples of the two forms. For normal samples and routine spectrometers these are not very useful, apart from the band at *ca.* 335 cm^{-1} which appears with a shoulder in spectra of form **B** and as two bands for form **A**. We found that the vibrations of form **B** at 485 and 750 cm^{-1} were split into two for form **A**, and used these diagnostically. Samples of form **B** obtained from alcoholic solutions and from CH_2Cl_2 solutions gave rise to identical IR spectra, except for the presence of ν(C–Cl) at 730 cm^{-1} in the latter. Care was taken to distinguish between these and form **A** (750 split into 755 and 745 cm^{-1}).

The ^{31}P-{^{1}H} NMR and UV/VIS spectra and the magnetic susceptibilities have been reported previously.[2] Forms **A** and **B** were not distinguishable by any of these techniques, nor by mass spectroscopy.

The X-ray powder diffraction data for form **A** and form **B** solvated with CH_2Cl_2 were different. From the published crystal structure data[4] a calculated powder pattern was generated, which closely matched the pattern of the solvated form **B**, thus identifying the form used by those authors. The results of the structure determination on a crystal of form **A** are summarised in Tables 1–3 and the molecular structure is shown in Fig. 1.

Since both forms crystallise in the space group $P2_1/c$ with $Z = 4$, then in each case the two phosphorus nuclei are crystallographically inequivalent and the solid-state ^{31}P NMR spectrum should consist of two resonances. This was indeed so. For form **A**, δ 55.3 and 52.2 and for the solvated form **B**, δ 61.9 and 60.0 (*cf.* $CHCl_3$ solution δ 58.2). Spectra were also obtained of form **B** (no CH_2Cl_2) and contained a somewhat broad resonance at about δ 64.6 and two much smaller resonances at δ 56.0 and 52.8.

Discussion

Using IR spectroscopy, Nakamoto and co-workers[3] distinguished between the two forms of [Ni(dppe)Cl_2]. We found that samples recrystallised from CH_2Cl_2 were more crystalline than crude samples, and gave rise to IR spectra which were identical with those of form **B**, apart from the additional band at 730 cm^{-1}. The recrystallized samples analyse as [Ni(dppe)Cl_2]·CH_2Cl_2. X-Ray powder diffraction data from these samples show them to have the same crystal structure as that previously reported for [Ni(dppe)Cl_2]·CH_2Cl_2.[4] This report gave no clues as to which form had been investigated. It can now be assigned as solvated form **B**.

Samples assigned by IR spectroscopy as form **B** (without CH_2Cl_2) gave rise to solid-state ^{31}P NMR spectra with small resonances obviously assignable to form **A**. The major resonance was broader, suggesting two unresolved signals, and shifted downfield relative to the resonances of solvated form **B**. These new data enable us to interpret the previously reported spectrum[2] as a mixture of form **B** (resonances at δ 66.5 and 65.1 resolved by resolution enhancement) and a high proportion of form **A** (δ 56.2 and 53.0). The IR spectrum of that sample appeared to be form **A**. Thus the solid-state NMR spectra have proved more successful than the IR spectra at distinguishing the two forms from each other, solvated from unsolvated and pure samples from mixtures. That samples assigned by IR spectroscopy as form **B** should give poorly resolved spectra and prove to contain some form **A** should perhaps be no surprise, as they are microcrystalline at best.

In order to try and understand the origin of the differences between the forms, the available crystal structures were compared using molecular graphics. We found that the crystal structure of the bromine analogue, [Ni(dppe)Br_2]·CH_2Cl_2,[12] superposes almost exactly on that of solvated form **B**[4] (there are some small differences in the positions of the dichloromethane molecules). This is as might be expected, since the unsolvated samples give rise to very similar IR spectra.[3]

Nakamoto and co-workers[3] suggested that the differences between the two forms of [Ni(dppe)Cl_2] could arise from different conformations of the chelate ring, or different orientations of the phenyl rings with both forms having the same chelate-ring conformation. We have found the latter to be the case. Both forms crystallise in space group $P2_1/c$, $Z = 4$, but since crystalline form **B** is the dichloromethane solvate it necessarily has a larger cell volume and a differing distribution of the cell contents. When the molecular structures of the two forms are displayed together (Fig. 2) it is evident that both have the δ chelate-ring conformation, but the phenyl-ring orientations differ considerably. With the nickel and phosphorus atoms constrained to be in the same place, the positions of the chelate ring carbon atoms differed by only 0.18 and 0.20 Å. In contrast, the phenyl-ring torsion angles differed by up to 78.1° [Ni–P(2)–C(211)–C(212), Table 3]. Spek *et al.*[4] noted that the molecule of form **B** has approximate non-crystallographic two-fold axial symmetry. This is illustrated by Fig. 3(*a*) where the

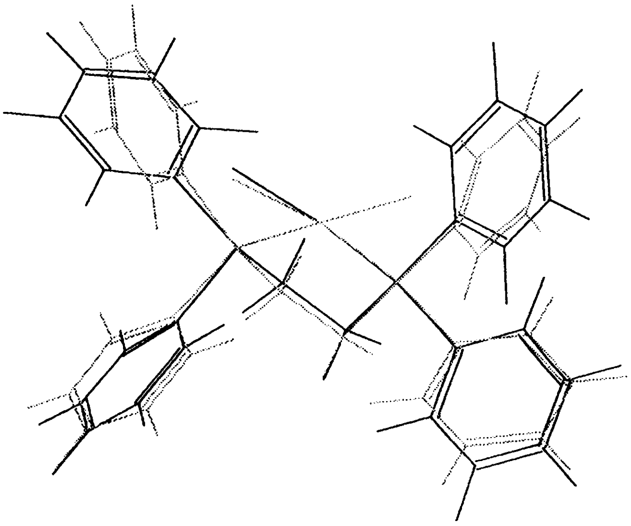

Fig. 2 Molecular structures of (. . .) form **A** and (—) form **B** of [Ni(dppe)Cl_2] drawn such that the Ni and P atoms from the two structures are coincident. The perspective has the P atoms towards the viewer, the Cl atoms away

Table 3 Selected bond lengths (Å), bond angles (°) and torsion angles (°) for [Ni(dppe)Cl_2] *

	Form A	Form B		Form A	Form B		Form A	Form B
Cl(1)–Ni	2.196(4)	2.195(2)	C(1)–P(1)	1.830(9)	1.829(5)	C(211)–P(2)	1.823(8)	1.807(5)
Cl(2)–Ni	2.203(4)	2.205(2)	C(2)–P(2)	1.843(9)	1.840(5)	C(221)–P(2)	1.820(7)	1.808(5)
P(1)–Ni	2.154(4)	2.157(2)	C(111)–P(1)	1.808(8)	1.808(5)	C(2)–C(1)	1.516(12)	1.523(7)
P(2)–Ni	2.153(4)	2.145(2)	C(121)–P(1)	1.813(8)	1.815(5)			
Cl(2)–Ni–Cl(1)	94.6(2)	95.47(6)	C(111)–P(1)–Ni	115.7(3)	110.8(2)	C(211)–P(2)–C(2)	103.7(4)	104.6(2)
P(1)–Ni–Cl(1)	89.1(2)	89.01(6)	C(111)–P(1)–C(1)	105.3(4)	105.2(2)	C(221)–P(2)–Ni	111.0(3)	111.2(2)
P(1)–Ni–Cl(2)	171.2(1)	175.19(6)	C(121)–P(1)–Ni	114.5(3)	119.2(2)	C(221)–P(2)–C(2)	102.1(4)	104.5(2)
P(2)–Ni–Cl(1)	175.2(1)	175.06(7)	C(121)–P(1)–C(1)	105.3(4)	105.0(2)	C(221)–P(2)–C(211)	110.4(3)	106.6(2)
P(2)–Ni–Cl(2)	89.5(2)	88.68(6)	C(121)–P(1)–C(111)	107.6(4)	106.1(2)	C(2)–C(1)–P(1)	107.0(6)	106.8(3)
P(2)–Ni–P(1)	87.3(2)	86.93(6)	C(2)–P(2)–Ni	109.2(3)	109.1(2)	C(1)–C(2)–P(2)	106.7(6)	107.1(3)
C(1)–P(1)–Ni	107.5(3)	109.5(2)	C(211)–P(2)–Ni	118.8(3)	119.6(2)			
Ni–P(1)–C(111)–C(112)	149.4	174.9	Ni–P(2)–C(211)–C(212)	22.7	100.8	Ni–P(2)–C(221)–C(222)	9.1	−6.3
Ni–P(1)–C(121)–C(122)	118.1	90.9						

* Data for form **B** taken from ref. 4.

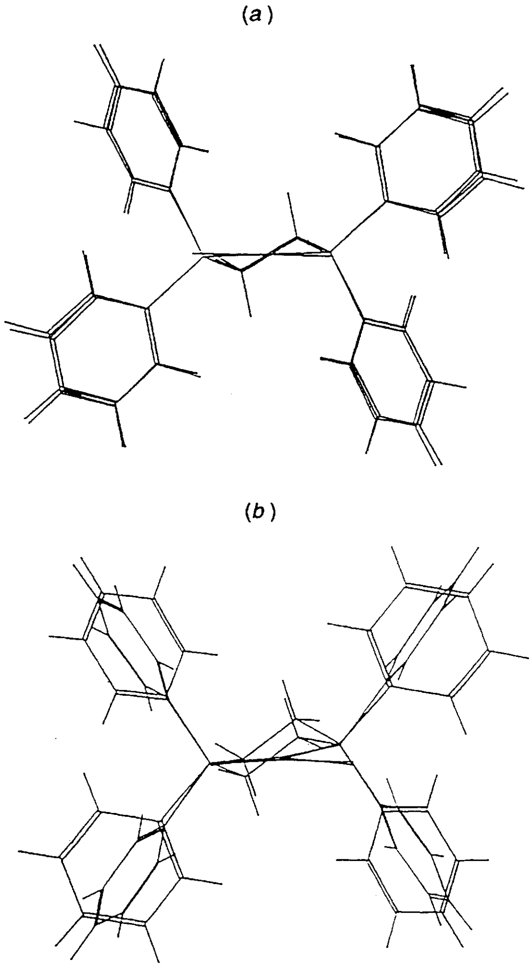

Fig. 3 Molecular structure of (*a*) form **B** and (*b*) form **A** of [Ni(dppe)Cl_2] rotated by 180° about the bisector of the Cl–Ni–Cl angle and drawn over the original molecule. This perspective has the Cl atoms towards the viewer, the P atoms away

molecule has been rotated by 180° about the bisector of the Cl–Ni–Cl angle and drawn over the original molecule. When the same procedure was carried out with the molecular structure of form **A**, the rotated drawing did not superpose on the original [Fig. 3(*b*)]; there is no two-fold axis. This then is the origin of the lower symmetry of form **A** which gives rise to the additional IR bands.

Conclusions

The crystal structure of form **A** of [Ni(dppe)Cl_2] has been determined and that published previously[4] shown to be solvated form **B**. The molecular structures differ in the orientations of the phenyl rings, which give rise to identifiable changes in the solid-state spectroscopic properties. Solid-state ^{31}P NMR spectra distinguished the two forms more reliably than did IR spectroscopy.

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References

1 R. D. McCullough and R. D. Lowe, *J. Chem. Soc., Chem. Commun.*, 1992, 70.
2 P. S. Jarrett and P. J. Sadler, *Inorg. Chem.*, 1991, **30**, 2098.
3 C. Udovich, J. Takemoto and K. Nakamoto, *J. Coord. Chem.*, 1971, **1**, 89.
4 A. L. Spek, B. P. van Eijck, R. J. F. Jans and G. van Koten, *Acta Crystallogr., Sect. C*, 1987, **43**, 1878.
5 K. Yvon, W. Jeitschko and E. J. Parthé, *J. Appl. Crystallogr.*, 1977, **10**, 73.
6 C. W. Lehmann, A. Karaulov and M. B. Hursthouse, *Z. Naturforsch., Teil A*, 1993, **48**, 63.
7 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.
8 N. G. Walker and D. Stuart, DIFABS, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
9 E. K. Davies, CHEM-X, Chemical Design Ltd., Oxford, 1991.
10 M. J. Hudson, R. S. Nyholm and M. H. B. Stiddard, *J. Chem. Soc. A*, 1968, 40.
11 G. R. van Hecke and W. de W. Horrocks, *Inorg. Chem.*, 1966, **5**, 1968.
12 J. A. Rahn, A. Delian and J. H. Nelson, *Inorg. Chem.*, 1989, **28**, 215.

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