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Tetrahedral cobalt(II) complexes stabilized by the aminodiphosphine PNP ligand [PNP = $CH_3CH_2CH_2N$-$(CH_2CH_2PPh_2)_2$]

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The reaction of $CoCl_2 \cdot 6H_2O$ and PNP [PNP = 1,1-bis(diphenylphosphinoethyl)-*n*-propylamine $(CH_3CH_2CH_2)$-$N(CH_2CH_2PPh_2)_2$] in ethanol affords the blue Co(II) complex [$CoCl_3\{\eta^1$-*P*$PPh_2CH_2CH_2N(CH_2CH_2CH_3)(H)$-$(CH_2CH_2P(O)Ph_2)\}$] (**1**), which has been characterized by spectroscopic methods and X-ray diffraction analysis. The structure of **1** consists of a tetrahedral cobalt atom coordinated by three chlorides and by an η^1-*P*-PNP ligand bearing a dangling P=O end and quaternised at the nitrogen atom. EPR measurements and a detailed analysis of the magnetic behaviour of **1** are consistent with a tetrahedral Co(II) ion and accordingly support the protonation of the PNP nitrogen atom. A mechanistic picture accounting for the formation of **1** has been proposed from the isolation and characterization of three reaction intermediates along the pathway leading to **1** which involve either η^2-*P*,*P*- and η^2-*P*,*N*-PNP cobalt complexes.

1 Introduction

Nitrogen-containing polyphosphines are an important class of polydentate ligands which exhibit different structural features and a variety of donor-ligand combinations.[1] These ligands have important applications in homogeneous catalysis and supramolecular chemistry and are the focus of current intense research interest.[2] Typical representatives of this class of ligands are the linear "PNP" aminodiphosphines $RN(CH_2$-$CH_2PR'_2)_2$ where an alkyl- or arylamine nitrogen atom is doubly connected *via* highly flexible ethylenic chains to two diorganyl phosphine ends.[3] "PNP" ligands combine two soft (P) and one hard (N) donor atoms, a non-rigid geometry, and the possibility to finely tune their steric and electronic requirements *via* modifying the bulkiness and the electron withdrawing/electron releasing properties of the groups on the phosphine ends. The potential chelation to the metal and the facility to generate coordination vacancies at the metal centre by alternating decoordination of either phosphorus or nitrogen donor represent a formidable *atout* to be exploited during a catalytic reaction. Consequently, "PNP" metal complexes are adequately designed for being included as fundamental ingredients in both catalytic and stoichiometric process.

Amongst the many reported "PNP"-type ligands, we have been interested in developing the coordination chemistry and the catalytic behaviour of transition-metal complexes containing the 1,1-bis(diphenylphosphinoethyl)-*n*-propylamine, hereafter PNP. This ligand was prepared in the early seventies by Morassi and Sacconi and used on a few occasions to assess five-coordination in first row transition metals.[4] A few years ago, some of us started an in-depth study aimed at investigating the chemistry and the catalytic hydrogenation aptitude of PNP iridium complexes[5] and described some PNP-based organo-ruthenium chemistry.[6] The latter studies afforded a wealth of interesting results, particularly in the area of metal–vinylidene[7] and –allenylidene reactivity.[8]

Following our results with 4d- and 5d-transition metals, we have decided to extend the boundary-line of the PNP chemistry towards first-row transition metal ions. Herein we present our results dealing with the chemistry of the PNP/cobalt system and a thorough magnetic characterisation of these systems, which proved of fundamental importance to assess the oxidation state of the metallic ion in the complex.

2 Experimental

All reagents and solvents were of analytical grade and were used without further purification. The ligand bis(diphenylphosphinoethyl)-*n*-propylamine, $CH_3CH_2CH_2N(CH_2CH_2$-$PPh_2)_2$ was prepared as described in the literature[9] and fully characterized by ^1H, $^{31}P\{^1H\}$, $^{31}C\{^1H\}$ NMR and elemental analyis. All reactions and manipulations were routinely performed in the air by using standard Erlenmayer flasks unless otherwise stated. The solid complexes were collected on Bückner- or Hirsch-type frits and washed with diethyl ether before being dried under vacuum. Deuterated chloroform for NMR measurements was purchased from Cortec (France) and dried over molecular sieves (0.4 nm). $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AVANCE DRX 300 spectrometer. Peak positions are relative to external 85% H_3PO_4 in D_2O with downfield values taken as positive. Infrared spectra were recorded on KBr discs using an IR-ATI Mattson Infinity Series. Uv-vis spectra were recorded with a HITACHI U-2000 spectrophotometer using *ca.* 1×10^{-3} M $CHCl_3$ solutions.

The magnetic susceptibility of a polycrystalline powder of **1** was measured between 2 and 300 K with applied magnetic fields of 0.1 and 1 Tesla using a Cryogenic S600 SQUID magnetometer. To avoid the orientation of polycrystalline powder which might eventually result in a much higher magnetic moment of the complex, the powder was pressed in a pellet. Data were corrected for the magnetism of the sample holder which was determined separately in the same temperature range

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and field, and the underlying diamagnetism of the sample was estimated from Pascal's constants. Magnetisation measurements were performed on the same sample at 2.3, 3.8 and 5.3 K with a field up to 6.5 Tesla.

Polycrystalline EPR powder spectra of **1** were recorded at X-band on a Varian E9 spectrometer equipped with a ^{4}He continuous flow cryostat.

Elemental analysis (C, H, N) were performed on a Fisons Instruments EA 1108 elemental analyser. The elemental analysis of cobalt was carried out by atomic absorption spectroscopy on a Perkin Elmer 5000 spectrophotometer. Chlorine was determined by volumetric titration with the method of Volhard after oxidative break-up of the sample.[10]

Synthesis of [$CoCl_3${$PPh_2CH_2CH_2N(CH_2CH_2CH_3)(H)$-($CH_2CH_2P(O)Ph_2$)-κ*P*}]·0.4EtOH (1·0.4EtOH)

Method A. A 50 mL Erlenmayer flask bearing a reflux condenser was charged with 10 mL of EtOH, solid PNP (0.30 g, 0.62 mmol) and $CoCl_2·6H_2O$ (0.30 g, 1.26 mmol) in the air. The mixture was stirred at room temperature for 20 min and then gently refluxed for 2 h. After this time, the periwinkle blue solution was cooled to room temperature and evaporated to half volume. Addition of acetone (10 mL) yielded blue microcrystals of **1**. Yield 83% (based on PNP).

IR/cm^{-1}): ν(C–H) 2968 (w), 2939 (w); ν(N–H) 2870–2470 (br w); δ(CH) 1472 (s), 1434 (s); ν(P=O) 1156 (s). UV/vis (DMSO), λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 614 (143), 678 (235). Anal. Calc. for $C_{31}H_{36}Cl_3CoNOP_2$·0.4EtOH (683.90): C, 55.8; H, 5.6; N, 2.0; Cl, 15.5; Co, 8.6. Found: C, 55.5; H, 5.8; N, 1.8; Cl, 15.1; Co, 8.2%.

Evaporation of the solvent from the filtered solution under reduced pressure, left a pale blue residue solid which was thoroughly washed with chloroform and diethyl ether to remove traces of **1** and organic compounds before being dried. The pale blue precipitate was dried under vacuum and identified as $Co(OH)Cl·5H_2O$ on the basis of elemental analysis and the IR spectrum. Yield: 39% (based on cobalt).

Method B. A 50 mL Erlenmayer flask bearing a reflux condenser was charged with solid PNP (0.10 g, 0.21 mmol), $CoCl_2·6H_2O$ (0.05 g, 0.21 mmol), NH_4Cl (0.013 g, 0.24 mmol) and 5 mL of EtOH and a stirring bar. The mixture was stirred while refluxing for 2 h and then cooled to room temperature. Slow evaporation of the blue solution and work up as above gave a crystalline crop of **1**. Yield: 79% (based on cobalt).

Method C. Replacing NH_4Cl with concentrated HCl (36.5%; 0.019 mL, 0.22 mmol) in the synthetic procedure described above afforded blue crystals of **1**. Yield: 82% (based on cobalt).

Synthesis of [$CoCl_2${$(CH_2CH_2CH_3)N(CH_2CH_2PPh_2)_2$-κ^2*P*,*P*}]·$H_2O$ (2·H_2O)

10 mL of EtOH were purged with nitrogen before adding solid PNP (0.3 g, 0.62 mmol) and $CoCl_2·6H_2O$ (0.15 g, 0.63 mmol) which yielded an emerald green solution. The solution was stirred and slowly brought to reflux which was maintained for 2 h. The green microcrystals of **2** which separated out, were collected on a sintered glass-frit and washed with H_2O (2 × 2 mL), EtOH (2 × 2 mL), Et_2O (2 × 2 mL) before being dried in the air. Yield: 78%. IR (cm^{-1}): ν(O–H) 3350 (m); ν(C–H) 2956 (m); δ(CH) 1483 (m), 1433(s). UV/vis ($CHCl_3$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 595 (309), 630 (311), 722 (381). Anal. Calc. for $C_{31}H_{37}Cl_2CoNOP_2$ (631.43): C, 59.0; H, 5.9; N, 2.2; Co, 9.3. Found: C, 59.7; H, 6.2; N, 1.9; Co, 9.1%.

Synthesis of [$CoCl_2${$PPh_2CH_2CH_2N(CH_2CH_2CH_3)CH_2CH_2P$-($O)Ph_2$-κ^2*P*,*N*}]·2$H_2O$ (3·2H_2O)

16 mL of air (*ca.* 0.15 mmol of O_2) were introduced with a tight-gas syringe into a stirred and degassed suspension of **2** (0.1 g, 0.15 mmol) in EtOH (5 mL) at room temperature. Immediately, the green colour of the **2** turned blue. Stirring was continued 60 min before removal of the solvent under vacuum to leave an azure powder, which was collected on a sintered glass-frit, washed with Et_2O (2 × 2 mL) and air dried. Yield: 90%. IR (cm^{-1}): ν(O–H) 3380 (m); ν(C–H) 2958, 2901, 2824 (w); δ(CH) 1435 (s); ν(P=O) 1158 (s). UV/vis ($CHCl_3$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 588 (399), 637 (426), 687 (314). Anal. Calc. for $C_{31}H_{39}Cl_2CoNO_3P_2$ (665.44): C, 55.9; H, 5.9; N, 2.1; Co, 8.9. Found: C, 56.3; H, 6.2; N, 2.1; Co, 8.5%.

Synthesis of [$CoCl_2${$(CH_2CH_2CH_3)(H)N(CH_2CH_2PPh_2)_2$-κ^2*P*,*P*}]Cl·2$H_2O$ (4·2H_2O)

Concentrated 36.5% HCl (30 μL, 0.30 mmol) was added at room temperature into an emerald green solution of **2** (0.1 g, 0.15 mmol) in degassed isopropanol (5 mL). The colour of the solution slightly darkened, but did not change appreciably. After 5 min stirring under nitrogen, slow addition of Et_2O (10 mL) left a green powder which was filtered out and washed with Et_2O (2 × 2 mL) before being dried in the air. Yield: 85%. UV-vis ($CHCl_3$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 595 (319), 632 (311), 723 (395). Anal. Calcd for $C_{31}H_{39}Cl_3CoNO_2P_2$ (684.90): C, 54.4; H, 5.7; N, 2.0; Co, 8.6. Found: C, 54.9; H, 6.0; N, 1.8; Co, 8.4%. IR (cm^{-1}): ν(O–H) 3360 (m); ν(C–H) 2956 (m); ν(N–H) 2870–2473 (br w); δ(CH) 1483 (m), 1433(s).

Reaction of 3 with HCl

A Schlenk-tube closed with a rubber septum was charged with solid **3** (0.10 g, 0.15 mmol) and 5 mL of EtOH purged with nitrogen to produce an azure solution. Addition of concentrated HCl (36.5%; 0.015 mL, 0.17 mmol) through the serum cap under vigorous stirring caused an immediate colour change to deep blue. Evaporation of the solvent to dryness under vacuum gave a periwinkle blue powder which was authenticated as **1** by elemental analysis and IR spectroscopy. Yield 95%.

Using NH_4Cl (9.1 mg, 0.17 mmol) instead of HCl in the above reaction caused a slow and irreversible change of the azure colour to periwinkle blue and afforded **1** in almost quantitative yield after 2 h stirring and usual work-up.

Reaction of 4 with oxygen

A Schlenck-tube topped with a rubber septum was charged with solid **4** (0.07 g, 0.10 mmol) and 5 mL of deaerated EtOH to give a clear green solution. Air was then admitted to the solution causing a quick colour change to deep blue. Work-up as above gave **1** in almost quantitative yield.

One pot transformation of 2 into 1

A stirred solution of **2** (50 mg, 75 μmol) and NH_4Cl (4.4 mg, 0.75 mmol) in 2 mL of EtOH was purged under nitrogen, warmed to *ca.* 50 °C and then exposed to air which caused a colour change from bright green to lime-green. Usual work-up provided **4** in *ca.* 87% yield.

Crystal data and structure refinement of [$CoCl_3${$PPh_2CH_2CH_2N$-($CH_2CH_2CH_3$)(H)($CH_2CH_2P(O)Ph_2$)-κ*P*}]·0.4 EtOH (1·0.4EtOH)

Blue crystals of **1·0.4EtOH** satisfactory for an X-ray analysis were obtained by filtering and slowly evaporating at room temperature in the air the blue solution obtained from method A described above. The crystal used for data collection was cut from a blue needle and gave rather broad diffraction peaks which has limited the quality of the refinement. Data were collected at 150(2) K on a Bruker SMART diffractometer, the data collection parameters are given in Table 1. The crystal structure was solved by direct methods using SHELXS-97[11] and refined by full matrix least squares with SHELXTL[12] using all the data.

Table 1 Crystal data and structure refinement for $[CoCl_3\{\eta^1\text{-}PPPh_2\text{-}CH_2CH_2N(CH_2CH_2CH_3)(H)(CH_2CH_2P(O)Ph_2)\}]\cdot 0.4EtOH$

Empirical formula	$C_{31.80}H_{38.40}Cl_3CoNO_{1.40}P_2$
Formula weight	684.26
Temperature/K	150(2)
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 29.860(5)$ Å, $\alpha = 90°$
	$b = 13.108(2)$ Å, $\beta = 130.973(2)°$
	$c = 22.394(4)$ Å, $\gamma = 90°$.
V/Å^3	6618.0(19)
Z	8
D_c/g cm^{-3}	1.374
μ/mm	0.885
$F(000)$	2843
Crystal size/mm	0.27 × 0.22 × 0.12
Crystal description	Blue block
θ range for data collection/°	1.80–25.00
Index ranges, hkl	−35 to 35, −15 to 15, −26 to 26
Reflections collected	31522
Independent reflections (R_{int})	5829 (0.0973)
Completeness to $\theta = 25.00°$ (%)	99.9
Absorption correction	Multiscan
Max. and min. transmission	0.928 and 0.720
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5829/510/427
Goodness-of-fit on F^2	1.074
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0750$, $wR2 = 0.2035$
R indices (all data)	$R1 = 0.1216$, $wR2 = 0.2367$
Largest diff. peak, hole/e Å^{-3}	1.828, −1.526

The partial-occupancy ethanol solvate was modelled with equal occupancy of two equivalent sites disordered about the 2-fold axis. One of the phenyl rings was also modelled over two overlapping orientations. All the non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms were inserted at calculated positions except for the hydrogen bound to N1, which was located from a difference map and not further refined, and the alcohol proton on the disordered, partial occupancy ethanol solvate, which was not included. There is some residual electron density in the region of the Co–P bond; attempts to apply disorder models or to reduce the symmetry did not improve the refinement.

CCDC reference number 210655.

See http://www.rsc.org/suppdata/dt/b3/b305443h/ for crystallographic data in CIF or other electronic format.

3 Results and discussion

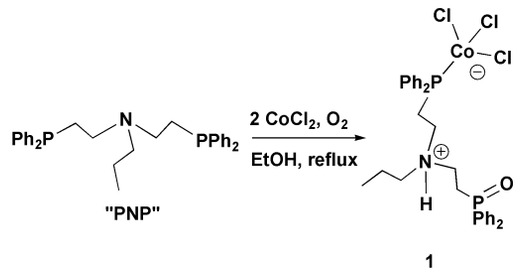
3.1 Reaction between PNP and $CoCl_2$ in the air. Synthesis and characterization of $[CoCl_3\{PPh_2CH_2CH_2N(CH_2CH_2CH_3)(H)(CH_2CH_2P(O)Ph_2)\text{-}\kappa P\}]$ (1)

The reaction of PNP with one equivalent of $CoCl_2\cdot 6H_2O$ in refluxing EtOH under aerobic conditions led to a blue solution from which blue microcrystals of the mononuclear complex $[CoCl_3\{PPh_2CH_2CH_2N(CH_2CH_2CH_3)(H)(CH_2CH_2P(O)Ph_2)\text{-}\kappa P\}]$ (**1**) were obtained in good yield while one equivalent of the ligand remains in solution ($^{31}P\{^1H\}$ NMR detected) (Scheme 1).

Addition of a third chloride equivalent, from either dilute hydrochloric acid or ammonium chloride, increased the yield of **1** almost to completeness while traces of PNP could not be detected in solution by NMR methods. Doubling the proportion of $CoCl_2$ had the same effect on the reaction consuming all the aminodiphosphine ligand and then providing the third equivalent of chloride necessary for the stabilization of **1**. In the latter reaction, half of the cobalt is not incorporated in the PNP complex and, after separation of **1**, may be recovered in the form of the hydroxo species $Co(OH)Cl\cdot 5H_2O$ as verified by IR spectroscopy and elemental analysis. This latter, repeated on three different samples obtained from independent reaction batches, provided an average Co : Cl ratio of *ca.* 0.9 well approaching the minimal formula of the hydroxo–chloride derivative.

Table 2 Selected bond lengths (Å) and angles (°) for $[CoCl_3\{\eta^1\text{-}PPPh_2\text{-}CH_2CH_2N(CH_2CH_2CH_3)(H)(CH_2CH_2P(O)Ph_2)\}]\cdot 0.4EtOH$

Co(1)–Cl(1)	2.2142(19)	Co(1)–P(1)	2.5160(20)
Co(1)–Cl(3)	2.2535(18)	P(2)–O(1)	1.4950(50)
Co(1)–Cl(2)	2.2575(17)		
Cl(1)–Co(1)–Cl(3)	114.43(7)	Cl(1)–Co(1)–P(1)	106.85(7)
Cl(1)–Co(1)–Cl(2)	116.73(7)	Cl(3)–Co(1)–P(1)	113.06(6)
Cl(3)–Co(1)–Cl(2)	108.50(7)	Cl(2)–Co(1)–P(1)	95.88(6)



Scheme 1

Blue well-shaped prismatic crystals of **1** suitable for an X-ray analysis were obtained as ethanol hemisolvate by slow evaporation of a warm ethanolic solution. The structure consists of discrete complex molecules and clathrated ethanol solvent molecules in 2 : 1 ratio. Selected bond lengths and angles are given in Table 2 while a drawing of the complex is shown in Fig. 1.

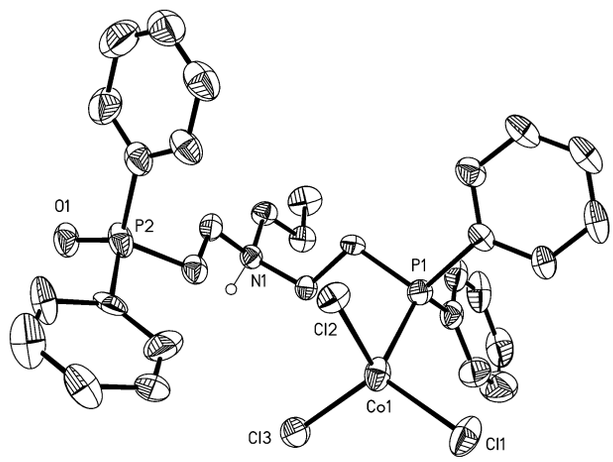


Fig. 1 Perspective view of **1** showing 40% atomic displacement ellipsoids. Hydrogen atoms have been omitted, except for the NH on the amine, and only one orientation of the disordered phenyl ring attached to P2 is shown.

The cobalt atom exhibits a slightly distorted tetrahedral geometry with PNP acting as a monodentate ligand through one phosphorus atom. The coordination tetrahedron about cobalt is completed by three chlorine atoms with an average Co–Cl separation of 2.2416 Å, This is consistent with the bond distances found in similar Co(II) chloride complexes. A search of the Cambridge structural database[13] revealed three Co(II) complexes with PCl_3 donor sets, all containing the $[Ph_3PCoCl_3]^-$ anion.[14] The closely-related five-coordinate complex trichloro-bis(triethylphosphine)cobalt(II) has also been reported.[15] The Co–Cl bond lengths all fall in the range 2.18–2.30 Å. The nitrogen donor atom of the aminodiphosphine lies far away from the metal centre ($d_{Co\cdots N} = 4.928(5)$ Å) and is probably quaternized (see below). One arm of the PNP ligand is uncoordinated and the phosphorus(III) group has been oxidized to phosphine oxide. Air oxidation of one P-donor atom of a polyphosphine is well documented[16] and has been crystallo-

graphycally ascertained for the tetrahedral cobalt complex $[\{NP_2(PO)\}Co(NO)_2]^+$ where the tripodal aminotriphosphine ligand acts as an κ^2P,P ligand $[NP_2(PO) = N(CH_2CH_2PPh_2)_2\text{-}\{CH_2CH_2P(O)Ph_2\}]$,[16a] but is unknown for linear aminodiphosphines like PNP.[17]

If one looks at the formula of **1**, a 3+ charge is required for balancing the complex to neutrality. Noticeably, if one additional positive charge was not present in the structure of **1**, we would be in the presence of a genuine Co(III) tetrahedral complex. This latter geometry is energetically highly disfavoured for d^6 ions in agreement with the predictions of the generally accepted bond theories for coordination compounds.[18] In keeping with this restriction, to the best of our knowledge, only a couple of pseudo-tetrahedral Co(III) complexes have been reported and structurally characterised,[19–20] and purely tetrahedral Co(III) centres have been spectroscopically characterised only within heteropolyanions of Keggin type.[21]

In the case at hand, a reasonable alternative to the existence of a Co(III) ion in **1** would be consistent with the formation of a conventional Co(II) species with the uncoordinated N-atom quaternised to form an ammonium salt. The presence of the N–H proton, although reasonably maintained from the solid-state dimeric aggregation of **1** (Fig. 2) and the N–OP separation between the closest molecules of 2.693(6) Å, could not be definitely confirmed by X-ray methods. In addition, an accurate inspection of the IR spectrum revealed only the presence of a broad and weak absorption between 2870–2470 cm^{-1}, that could not be assumed as a unquestionable proof for the presence of the quaternized amine.[22] Finally, there is no simple explanation to account for the protonation of the PNP-N atom in the experimental conditions leading to **1**. The protonation of the PNP amine in boiling ethanol is unprecedented for both the free ligand and its complexes with transition metals.

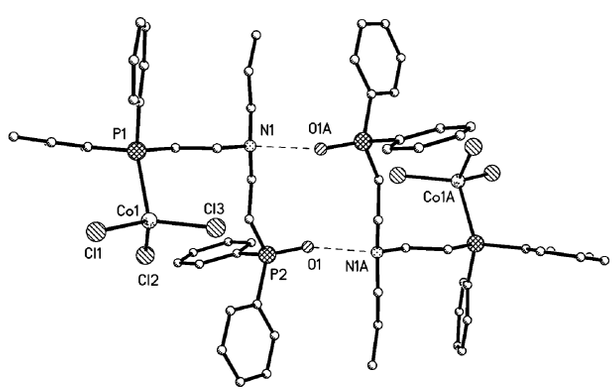


Fig. 2 Perspective view of the dimeric unit in **1**, the hydrogen bonds are shown as dotted lines.

To definitely determine the oxidation state of the cobalt centre in **1**, we decided to investigate its magnetic behaviour. Whenever we were in presence of a Co(III) centre an $S = 2$ ground state was expected, while a tetrahedral Co(II) would result in a ground $S = 3/2$ state, so that the room-temperature magnetic moment in the two cases should help in assigning the oxidation states. The low-temperature magnetic behaviour constitutes a further criterion to discriminate between the two oxidation states. Indeed, while Co(II) is a Kramers ion and should then show an EPR signal for any value of the zero field splitting, the large zero field splitting expected for the $S = 2$ ground state of Co(III) should hamper the detection of EPR signal. Indeed these kinds of systems are well known to be silent at X-band and, until the advent of high field/high frequency EPR spectroscopy,[23] only with parallel mode detection has it been possible to extract information concerning their spin Hamiltonian parameters.[24] As we will show in the following section, our study unequivocally proved that we were in presence of a genuine Co(II) species.

3.2 Magnetic measurements

Powder susceptibility measurements (Fig. 3) of **1** evidenced a room temperature value of $\mu_{eff} = 4.68\ \mu_B$; this value is lower than that characterising a tetrahedral Co(III) for which a value of $\mu_{eff} = \mu_{s.o.}(1 - 2\lambda/Dq) \approx 5.1\ \mu_B$ (where Dq is the ligand field strength and $\mu_{s.o.}$ the expected spin-only value for the magnetic moment) is expected.[25] On the other hand, for a tetrahedral Co(II) which has an orbital singlet $^4A_{1g}$ ground state, the obtained value is in the higher limit of the expected range for this coordination geometry[26,27] and higher than that measured for a series of phosphine–halide tetrahedral Co(II) complexes reported by Gerloch *et al.*[27] The decreasing of the magnetic moment observed on lowering temperature below 50 K can be attributed to the zero field splitting of the ground multiplet.

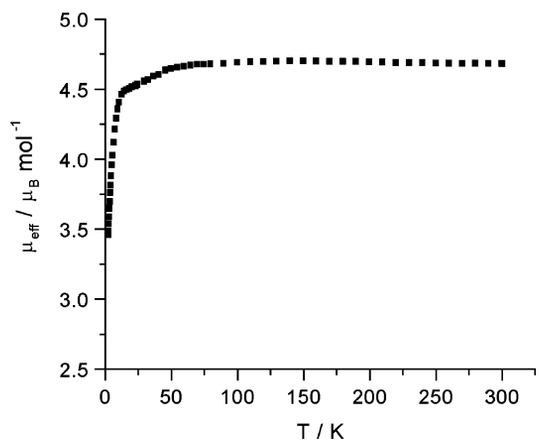


Fig. 3 Temperature variation of the magnetic moment of **1** between 2 and 300 K.

The X-band EPR spectrum of **1** recorded at low temperature, shown in Fig. 4, could be interpreted within the framework of an effective ground spin doublet with a very anisotropic g factor, which is the result of a large zero field splitting of the $S = 3/2$ multiplet. Indeed, a quite satisfactory simulation of the spectrum was obtained by imposing $g_x = 5.03$, $g_y = 3.62$, $g_z = 2.21$, $S_{eff} = 1/2$. As mentioned above, if the cobalt ions were in tripositive oxidation state, no EPR spectrum would have been expected at this frequency and field.

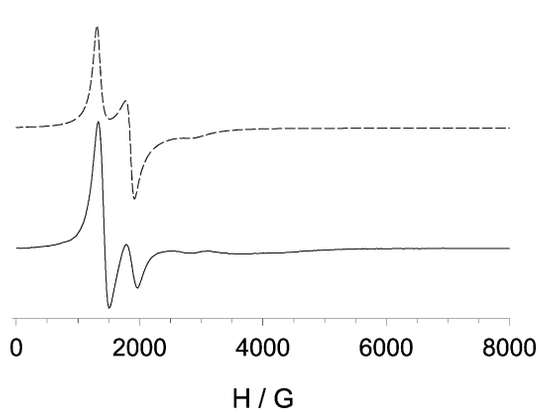


Fig. 4 Experimental (continuous line) and simulated (dashed line) powder X-Band EPR spectra of **1** at 4.2 K. The discrepancy in the lineshapes and relative intensities between the simulated and experimental spectra may be attributed to a partial orientation of the sample.

The obtained g values for the effective ground doublet could be rationalised on the basis of the Angular Overlap Model, implemented by a program which has been described elsewhere.[28] The electronic parameters to describe the ligand field around the cobalt ion were adapted by literature data to obtain

the best agreement with the results obtained by the analysis of the EPR spectrum. The best fit parameters were e_σ(Cl) = 3600 cm^{-1} e_σ(P) = 4000 cm^{-1}, e_π(Cl) = 400 cm^{-1}, e_π(P) = −2000 cm^{-1}, k = 0.9, ζ = 530 cm^{-1} which fall in the range previously determined for tetrahalogeno-[29] and dihalogeno-bisphosphine[27] cobaltate complexes. By using the Gerloch formula[30] to describe the system in terms of an effective spin doublet, the obtained g values were g_x = 2.08, g_y = 3.71, g_z = 5.10, while the splitting between the ground doublet and the first excited one was calculated to be 17.26 cm^{-1}. This description was finally confirmed by magnetisation *vs.* field measurement performed at three different temperatures (Fig. 5). The three experimental curves could be reproduced with a unique set of parameters on the basis of the spin Hamiltonian relative to the quartet state [eqn. (1)]:

$$\boldsymbol{H} = D[S_z^2 + E/D(S_x^2 - S_y^2)] + \mu_B \boldsymbol{S g B} \qquad (1)$$

by imposing D = + 8.5 cm^{-1}, E/D = 0.1 and g_{av} = 2.39. With these parameters the splitting at zero field between the M_s = ± 1/2 (lying lowest) and the M_s = ±3/2 one is of 17.35 cm^{-1}, in very good agreement with the results of AOM calculation. Furthermore, with the average g value obtained by these simulations, a room-temperature magnetic moment μ_{eff} = 4.62 μ_B is expected, quite close to the measured value (see above). We may then conclude that the analysis of the magnetic data could ultimately assess the bipositive oxidation state of the Co ion in **1** and thus unequivocally confirmed the protonation of the nitrogen atom of the PNP ligand.

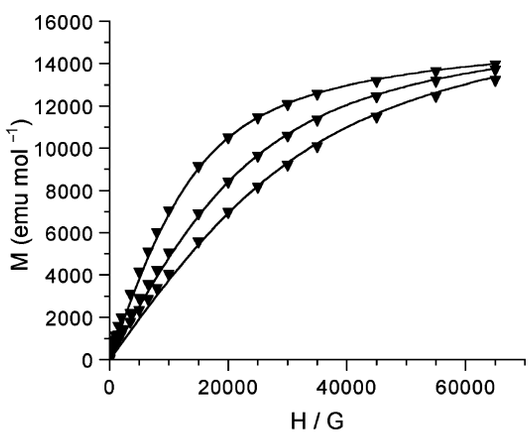


Fig. 5 Experimental magnetisation curves (inverse triangles) for **1** recorded at 2.3, 3.8 and 5.3 K, respectively, together with the best simulated curves. See text for details.

3.3 Reaction between PNP and $CoCl_2$ under inert atmosphere

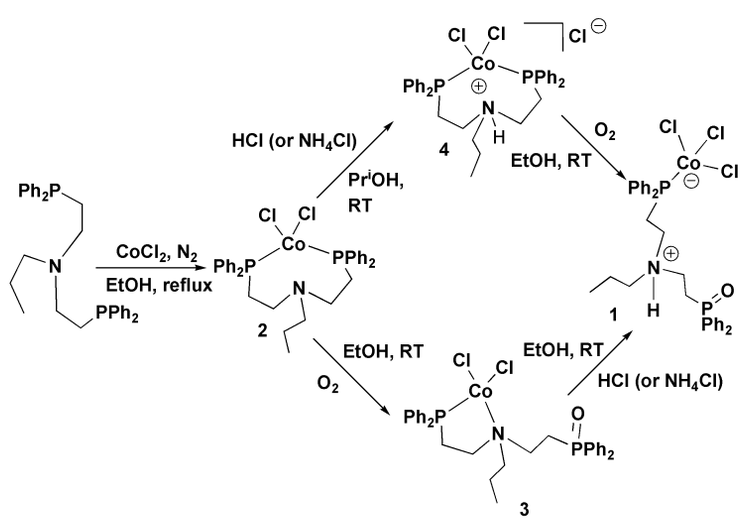
In order to shed some light to the formation of **1** from PNP and cobalt chloride, we decided to investigate how the PNP ligand combines with cobalt(II) ions under inert atmosphere. The reaction of the aminodiphosphine with $CoCl_2 \cdot 6H_2O$ in ethanol under nitrogen took place slowly at room temperature, but quickly at reflux, leading to a green solution from which emerald green microcrystals of [$CoCl_2${($CH_2CH_2CH_3$)N(CH_2-CH_2PPh_2)$_2$-κ^2*P*,*P*}] (**2**) precipitated in 2 h at room temperature (Scheme 2). The elemental analysis suggested that, at variance with **1**, **2** contained an 1 : 2 Co : Cl ratio.

Although it was not possible to grow crystals suitable for a crystallographic analysis, we assigned to **2** a tetrahedral geometry with the metal coordinated by two chlorides and the two PNP phosphorus atoms. The structural assignment followed safely from the analysis of the UV-vis spectrum showing the absorptions expected for a Co(II) ion in a tetrahedral environment.[31] The absence of any visible ^{31}P NMR signal in the region of the uncoordinated PNP phosphorus atoms represents a further assist in favour of *P*,*P*-coordination, even if the paramagnetism of this complex could be also responsible for the missing NMR information from the ^{31}P NMR spectrum.

Complex **2** is air stable in the solid state. However, addition of one equivalent of oxygen with a tight-gas syringe into a stirred EtOH suspension of **2**, caused an immediate colour change from emerald green to azure. Solvent evaporation gave [$CoCl_2${$PPh_2CH_2CH_2N(CH_2CH_2CH_3)CH_2CH_2P(O)Ph_2$-κ^2*P*,*N*}] (**3**) as an azure powder in good isolated yield (Scheme 2). Elemental analysis, UV-vis and IR spectroscopy suggested that **3** was a tetrahedral Co(II) complex containing two chlorides and a *P*,*N*-bidentate PNP ligand chelating the metal with the nitrogen and one phosphorus atoms. The other P-atom was oxidised ($\nu_{(P=O)}$ 1158 cm^{-1}) and therefore not engaged in the coordination polyhedron around cobalt. The ^{31}P{^{1}H} NMR spectrum showed the presence of a broad resonance at *ca.* 20.0 ppm ($CDCl_3$, room temperature) ascribable to the dangling oxidised phosphine arm while the other coordinated phosphorus atom does not provide any observable resonance as a consequence of the paramagnetism of the complex responsible for its fast relaxation.[32]

Complex **3** is air stable in both solid state and ethanolic solution, but immediately reacts with hydrochloric acid to afford **1** in quantitative yield (Scheme 2). The conversion of **3** into **1** takes place also in the presence of chloride sources other than HCl, but the transformation is slower at room temperature.

The stepwise transformation of **2** into **1** could be also accomplished by inverting the order by which oxygen and



Scheme 2

chloride are added to the PNP/Co system. Thus, when a warm solution of **2** was firstly reacted with HCl and then exposed to air, a straightforward transformation to the final blue product **1** was observed (Scheme 2). Remarkably, the transformation of **2** into **1** occurred *via* a two-step mechanism with formation of an intermediate species which could be intercepted in the absence of oxygen. Therefore, treatment of **2** with HCl under nitrogen in either $CHCl_3$ or EtOH and work-up of the resulting green solution provided lime-coloured crystals of the N-protonated complex $[CoCl_2\{(CH_2CH_2CH_3)(H)N(CH_2CH_2PPh_2)_2\text{-}\kappa^2P,P\}]Cl$ (**4**) in *ca*. 85% yield. Exposure of a solution of **4** in EtOH to air quickly and irreversibly changed the colour to blue affording quantitatively **1**. On transforming **2** into **4**, the only significant change in the IR spectrum was the appearance of a broad absorption extending from 2870 to 2473 cm^{-1}. Such a finding may be indirectly assumed as a reliable proof of N-detachment also in the parent complex **2**

4 Conclusion

We have successfully prepared monometallic cobalt(II) complexes of the flexible aminodiphosphine PNP [PNP = $CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$]. The complex $[CoCl_3\{PPh_2CH_2CH_2N(CH_2CH_2CH_3)(H)(CH_2CH_2P(O)Ph_2)\text{-}\kappa P\}]$ (**1**) was obtained by refluxing $CoCl_2$ and PNP in ethanol. It was characterised as a genuine Co(II) tetrahedral complex by conventional spectroscopic methods and X-ray diffraction analysis. In the reaction one of the P-end of the PNP ligand is oxidised to phosphine oxide while the uncoordinated N-atom is quaternised. An in-depth study of the magnetic behaviour of **1** confirmed the bipositive oxidation state of the cobalt ion.

The stepwise formation of **1** has been demonstrated by solution studies under both anaerobic and aerobic conditions and through the interception of reaction intermediates which have been experimentally demonstrated to be precursors of **1**.

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References

1 (*a*) J.-C. Hierso, R. Amardeil, E. Bentabet, R. Broussier, B. Gautheron, P. Meunier and P. Kalck, *Coord. Chem. Rev.*, 2003, **236**, 143; (*b*) F. A. Cotton and B. Hong, *Prog. Inorg. Chem.*, 1992, **40**, 179; (*c*) H. A. Mayer and W. C. Kaska, *Chem. Rev.*, 1994, **94**, 1239.

2 (*a*) P. Espinet and K. Soulantica, *Coord. Chem. Rev.*, 1999, **193/195**, 499; (*b*) M. D. Fryzuk, T. S. Haddad and D. J. Berg, *Coord. Chem. Rev.*, 1990, **99**, 137; (*c*) M. D. Fryzuk and C. D. Montgomery, *Coord. Chem. Rev.*, 1989, **95**, 1; (*d*) P. Bhattacharyya and J. D. Woollins, *Polyhedron*, 1995, **14**, 3367; (*e*) C. Bianchini, A. Meli, M. Peruzzini, F. Vizza and F. Zanobini, *Coord. Chem. Rev.*, 1992, **120**, 193; (*f*) L. Crociani, F. Tisato, F. Refosco, G. Bandoli, B. Corain and L. M. Venanzi, *J. Am. Chem. Soc.*, 1998, **120**, 2973; (*g*) A. N. Ajjou and H. Alper, *J. Am. Chem. Soc.*, 1998, **120**, 1466; (*h*) M. Qadir, T. Möchel and K. K. Hii, *Tetrahedron*, 2000, **56**, 1320; (*i*) T. Mizugaki, M. Murata, M. Ooe, K. Ebitani and K. Kaneda, *Chem. Commun.*, 2002, 52.

3 (*a*) M. M. Taqui Khan and V. V. Sen Reddy, *Inorg. Chem.*, 1986, **25**, 208; (*b*) L. Sacconi, C. A. Ghilardi, C. Mealli and F. Zanobini, *Inorg. Chem.*, 1975, **14**, 1380; (*c*) M. M. Taqui Khan, P. Paul, K. Venkatasubramnian and S. Purokit, *J. Chem. Soc., Dalton Trans.*, 1991, 3405; (*d*) M. M. Taqui Khan and E. R. Rao, *Polyhedron*, 1987, **6**, 1727; (*e*) M. M. Taqui Khan, V. V. Sen Reddy and H. C. Bajaj, *Inorg. Chim. Acta.*, 1987, **130**, 163; (*f*) M. M. Taqui Khan, V. V. Sen Reddy and H. C. Bajaj, *Polyhedron*, 1987, **6**, 921; (*g*) M. M. Taqui Khan, H. C. Bajaj, M. R. H. Siddiqui, B. T. Khan, M. S. Reddy and K. V. Reddy, *J. Chem. Soc., Dalton Trans.*, 1985, 2603; (*h*) K. K. Hii, M. Thornton-Pett, A. Jutand and R. P. Tooze, *Organometallics*, 1999, **18**, 1887; (*i*) R. G. Nuzzo, S. L. Haynie, M. E. Wilson and G. M. Whitesides, *J. Org. Chem.*, 1981, **46**, 2681; (*j*) M. S. Rahman, J. W. Steed and K. K. Hii, *Synthesis*, 2000, 1320; (*k*) M. M. Taqui Khan and V. V. Sen Reddy, *Inorg. Chem.*, 1986, **25**, 208; (*l*) N. Margotta, A. Habtemariam and P. J. Sadler, *Angew. Chem., Int. Ed.*, 1997, **36**, 1185; (*m*) D. Walther, T. Döhler, K. Heubach, O. Klobes, B. Schweder and H. Görls, *Z. Anorg. Allg. Chem.*, 1999, **625**, 923; (*n*) M. I. García-Sejo, A. Habtemariam, S. Parsons, R. O. Gould and M. E. García-Fernández, *New J. Chem.*, 2002, **26**, 636.

4 (*a*) L. Sacconi and R. Morassi, *J. Chem. Soc. A*, 1968, 2997; (*b*) R. Morassi and L. Sacconi, *J. Chem. Soc. A*, 1971, 492; (*c*) A. Bianchi, P. Dapporto, G. Fallani, C. A. Ghilardi and L. Sacconi, *J. Chem. Soc., Dalton Trans.*, 1973, 1973; (*d*) M. Di Vaira, S. Midollini and L. Sacconi, *Inorg. Chem.*, 1978, **17**, 816; (*e*) P. L. Orioli and C. A. Ghilardi, *J. Chem. Soc. A*, 1970, 1511.

5 (*a*) C. Bianchini, E. Farnetti, M. Graziani, G. Nardin, A. Vacca and F. Zanobini, *J. Am. Chem. Soc.*, 1990, **112**, 9190; (*b*) E. Farnetti, N. Verma and M. Graziani, *Gazz. Chim. Ital.*, 1993, **123**, 165; (*c*) C. Bianchini, M. Peruzzini, E. Farnetti and J. Kaspar, *J. Organomet. Chem.*, 1995, **488**, 91; (*d*) C. Bianchini, E. Farnetti, L. Glendenning, M. Graziani, G. Nardin, M. Peruzzini, E. Rocchini and F. Zanobini, *Organometallics*, 1995, **14**, 1489.

6 (*a*) C. Bianchini, P. Innocenti, D. Masi, M. Peruzzini and F. Zanobini, *Gazz. Chim. Ital.*, 1992, **122**, 461; (*b*) C. Bianchini, D. Masi, M. Peruzzini, A. Roemrosa and F. Zanobini, *Acta Crystallogr., Sect. C*, 1995, **51**, 2514; for a recent paper describing some coordination compounds of ruthenium with PNP ligands, see: M. S. Rahman, P. D. Prince, J. W. Steed and K. K. Hii, *Organometallics*, 2002, **21**, 4927.

7 (*a*) C. Bianchini, L. Glendenning, M. Peruzzini, A. Romerosa and F. Zanobini, *Chem. Commun.*, 1994, 2219; (*b*) C. Bianchini, P. Innocenti, M. Peruzzini, A. Romerosa and F. Zanobini, *Organometallics*, 1996, **15**, 272; (*c*) C. Bianchini, J. A. Casares, M. Peruzzini, A. Romerosa and F. Zanobini, *J. Am. Chem. Soc.*, 1996, **118**, 4585; (*d*) C. Bianchini, M. Peruzzini, G. Purches and F. Zanobini, *Inorg. Chim. Acta*, 1998, **272**, 1; C. Bianchini, M. Peruzzini, D. Masi, A. Romerosa and F. Zanobini, *Organometallics*, 1999, **18**, 2376.

8 C. Bianchini, M. Peruzzini, F. Zanobini, C. Lopez, I. de los Ríos and A. Romerosa, *Chem. Commun.*, 1999, 443; C. Bianchini, C. Lopez, I. de los Ríos, M. Peruzzini and A. Romerosa, *J. Organomet. Chem.*, 2000, **593/594**, 485.

9 L. Sacconi and R. Morassi, *J. Chem. Soc. A*, 1969, 2904.

10 J. Volhard, *J. Prakt. Chem.*, 1874, **117**, 217.

11 SHELXS-97, G. M. Sheldrick, University of Göttingen, Germany, 1997.

12 G. M. Sheldrick, SHELXTL version 5.1, Bruker-AXS, Madison, WI, USA, 1998.

13 F. H. Allen, *Acta Crystallogr., Sect. B*, 2002, **58**, 390–388; D. A. Fletcher, R. F. McMeeking and D. Parker, *J. Chem. Inf. Comput. Sci.*, 1996, **36**, 746–749.

14 (*a*) D. Fenske, R. Basoglu, J. Hachgenei and F. Rogel, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 160; (*b*) D. Fenske, J. Ohmer and K. Merzweiler, *Z. Naturforsch., Teil B*, 1987, **42**, 803; (*c*) G.-Q. Li, F.-K. Zheng, G.-C. Guo and J.-S. Huang, *Jiegou Huaxue (in Chinese) (J. Struct. Chem.)*, 2000, **19**, 230.

15 W. J. P van Enckevort, H. M. Hendricks and P. T. Beurskens, *Cryst. Struct. Commun.*, 1977, **6**, 531.

16 (*a*) C. A. Ghilardi and L. Sacconi, *Cryst. Struct. Commun.*, 1976, **4**, 687; (*b*) R. Rossi, L. Marvelli, A. Marchi, L. Magon, V. Bertolasi and V. Ferretti, *J. Chem. Soc., Dalton Trans.*, 1994, 339; (*c*) K. Heinze, G. Huttner and L. Zsolnai, *Chem. Ber.*, 1997, **130**, 1393; (*d*) V. Bertolasi, C. Bianchini, I. de los Rios, L. Marvelli, M. Peruzzini and R. Rossi, *Inorg. Chim. Acta*, 2002, **327**, 140.

17 Bis(phosphino)amines with short-bite "PNP" backbones, $RN(PR'_2)_2$, can be easily oxidized at one phosphorus atom to form a series of heterofunctional, P,O ligands with a soft P(III) and a relatively harder phosphine oxide center. See: (*a*) A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1996, 1283; (*b*) A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1996, 4575; (*c*) M. B. Smith, A. M. Z. Slawin and J. D. Woollins, *Polyhedron*, 1996, **15**, 1579; (*d*) M. B. Smith and A. M. Z. Slawin, *Inorg. Chim. Acta*, 2000, **299**, 172.

18 B. N. Figgis, 'Ligand Field Theory', in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, UK, 1st edn., 1987, vol. 1, pp. 213–281.

19 H. Doerrer, M. T. Bautista and S. J. Lippard, *Inorg. Chem.*, 1997, **36**, 3578.

20 C. Dehnen and C. Zimmermann, *Eur. J. Inorg. Chem.*, 2000, 1471.

21 K. Kojima, J. Matsuda, N. Kojima, T. Ban and I. Tsujikawa, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 3213.
22 A. J. Gordon and R. A. Ford, *The Chemist's Companion*, John Wiley & Sons, Inc, 1st edn., 1972, p. 193.
23 D. Gatteschi, L. Sorace, R. Sessoli and A. L. Barra, *Appl. Magn. Reson.*, 2001, **21**, 299.
24 H. J. Gerritsen and E. S. Sabisky, *Phys. Rev.*, 1963, **132**, 1507.
25 E. A. Boudreax and L. N. Mulay, *Theory and Application of Molecular Paramagnetism*, Wiley, New York, 1976.
26 B. Chiari, A. Cinti, O. Crispu, F. Demartin, A. Pasini and O. Piovesana, *J. Chem. Soc., Dalton Trans.*, 2001, 3611.
27 J. E. Davies, M. Gerloch and D. J. Phillips, *J. Chem. Soc., Dalton Trans.*, 1979, 1836.
28 W. D. Horrocks and D. A. Burlone, *J. Am. Chem. Soc.*, 1976, **98**, 6512.
29 A. Bencini, I. Ciofini and M. G. Uytterhoeven, *Inorg. Chim. Acta*, 1998, **274**, 90.
30 M. Gerloch and R. F. McMeeking, *J. Chem. Soc., Dalton Trans.*, 1975, 2443.
31 D. Sutton, *Electronic Spectra of Transition Metal Complexes*, Mc Graw-Hill, Maidenhead, Berkshire, England, 1975; A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, New York, 2nd edn., 1984, pp. 480–505.
32 See, for example: X. R. L. Fontaine, E. H. Fowles, T. P. Layzell, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1991, 1619.