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Synthesis, structure and properties of mononuclear cobalt(II) and cobalt(III) pseudohalide complexes containing N-donor Schiff bases: Synthetic control of metal oxidation levels

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Abstract

Two different series of cobalt(II) and cobalt(III) complexes of types $[Co(L^1)(X)_2]$ (**1a**–**1f**) and $[Co(L^2)(X)_3]$ (**2a**–**2f**), respectively [L^1 = *N*,*N*′-(bis(pyridin-2-yl)formylidene)propane-1,3-diamine (pfpd) or *N*,*N*′-(bis(pyridin-2-yl)benzylidene)propane-1,3-diamine (pbpd); L^2 = (*N*,*N*-diethyl,*N*′-(pyridin-2-yl)formylidene)ethane-1,2-diamine (pfed) or (*N*,*N*-diethyl,*N*′-(pyridin-2-yl)benzylidene)-ethane-1,2-diamine (pbed); X = N_3^-, NCS^- or NCO^-] have been prepared and characterized using microanalytical, spectroscopic, magnetic, electrochemical and other physicochemical results. Structures of one member in each series, viz., $[Co(pfpd)(NCS)_2]$ (**1c**) and $[Co(pbed)(N_3)_3]$ (**2b**) are solved by X-ray diffraction measurements for the exact definition of the coordination sphere. Structural analysis reveals cobalt(II) centre in **1c** adopts a distorted octahedral environment with a CoN_6 chromophore ligated by four N atoms of the tetradentate Schiff base and two N-coordinated NCS^- ions in *trans* orientation. In **2b**, the three N atoms of the tridentate Schiff base and three N atoms of three terminal azides are found in *meridional* arrangement. The organic blockers are folded in ethylenic/propylenic part. Electrochemiocal electron transfer study in MeCN solutions shows cobalt(III)–cobalt(II) response as oxidative in **1** and reductive in **2**. Available information shows that the structures **1a**, **1b**, **1d**–**1f** are cognate with **1c**, whereas **2a**, **2c**, **2d**–**2f** are iso-structural with **2b**. All the complexes display intraligand $^1(\pi–\pi^*)$ fluorescence and intraligand $^3(\pi–\pi^*)$ phosphorescence in glassy solutions (MeOH at 77 K).

Keywords: Cobalt(II)/cobalt(III) compounds; Schiff bases; X-ray structures; Electrochemistry; Luminescence

1. Introduction

Research on design and synthesis of mono- and polynuclear coordination [1–3] compounds of cobalt in its varied oxidation levels continues unabated for different uses [4–7]. Exploiting the various coordination environments around the metal centre, different geometries may be accessed using varied organic blockers and bridging units. Self-assembly [8] is the most efficient approach towards preparation of such materials. We are also active [9–11] in this field particularly with pseudohalides and Schiff bases. Pseudohalides [12] have long been known for their versatile coordination modes to give monomeric, dimeric and polymeric complexes. Schiff bases [9,13] are useful chelators because of their preparative accessibilities, structural varieties and varied denticities. Cobalt is well suited [1] to this study as it permits a wide range of symmetries and coordination numbers in its

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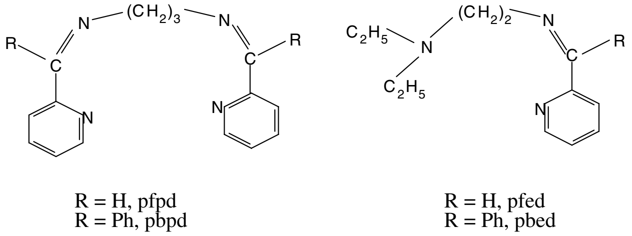

Scheme 1.

different oxidation states. We have successfully isolated six cobalt(II) and six cobalt(III) mononuclear complexes of the types $[Co(L^1)(X)_2]$ (**1a**–**1f**) and $[Co(L^2)(X)_3]$ (**2a**–**2f**) [L^1 = *N*,*N*′-(bis(pyridin-2-yl)formylidene)propane-1,3-diamine (pfpd) or *N*,*N*′-(bis(pyridin-2-yl)benzylidene)propane-1,3-diamine (pbpd); L^2 = (*N*,*N*-diethyl, *N*′-(pyridin-2-yl)formylidene)ethane-1,2-diamine (pfed) or (*N*,*N*-diethyl,*N*′-(pyridin-2-yl)benzylidene)ethane-1,2-diamine (pbed), Scheme 1; $X = N_3^-$, NCS^- or NCO^-] using one-pot reactions of cobalt(II) salt, L and pseudohalide in 1:1:2 and 1:1:3 molar ratios, respectively, at room temperature in methanol–water solvent mixtures. All the complexes are characterized using microanalytical, spectroscopic, magnetic, electrochemical and other physicochemical results. In two representative cases, $[Co(pfpd)(NCS)_2]$ (**1c**) and $[Co(pbed)(N_3)_3]$ (**2b**), crystal structures have been solved by X-ray diffraction measurements to define the coordination spheres. This paper has addressed the details of syntheses, structures and properties of these new complexes and focused on the stabilization of metal oxidation levels through judicious choice of Schiff base-pseudohalide combinations.

2. Experimental

2.1. Materials

High purity 2-benzoylpyridine (Lancaster, UK), pyridine-2-carboxaldehyde (Lancaster, UK), *N*,*N*-diethylethane-1,2-diamine (SRL, India), propane-1,2-diamine (SRL, India), cobalt nitrate hexahydrate (E. Merck, India), sodium azide (E. Merck, India), ammonium thiocyanate (E. Merck, India), and sodium cyanate (Lancaster, UK) were used as received. Cobalt perchlorate hexahydrate was prepared on treatment of cobalt carbonate (E. Merck, India) with perchloric acid (E. Merck) followed by slow evaporation on a steam bath, filtration through a fine glass-frit and preservation in a desiccator containing concentrated sulphuric acid (E. Merck, India) for subsequent use. Purification of MeCN and preparation of supporting electrolyte ($[Et_4N][ClO_4]$) for electrochemical work were executed following reported method [14]. All other chemicals were of analytical grade and were used without further purification.

Caution! Perchlorate and azide compounds of metal ions are potentially explosive especially in presence of organic ligands. Only a small amount of the materials should be prepared and handled with care.

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin–Elmer 2400 CHNS/O elemental analyzer. IR spectra (KBr discs, 4000–300 cm^{-1}) were recorded using a Jasco FT-IR Model 420 spectrometer. Molar conductances were measured using a Systronics conductivity meter where the cell constant was calibrated with 0.01 M KCl solution and dry MeCN was used as solvent. Room-temperature magnetic susceptibilities of powder samples were done on a PAR 155 vibrating sample magnetometer, with $Hg[Co(SCN)_4]$ as the reference. Diamagnetic corrections were made using Pascal's constants. Ground state absorption and steady-state fluorescence measurements were made with a Jasco Model V-530 UV–Vis spectrophotometer and Hitachi Model F-4010 spectrofluorimeter, respectively. Time-resolved fluorescence measurements were carried out using a time-correlated single photon counting (TCSPC) spectrometer Edinburgh Instruments, Model 199; hydrogen filled coaxial flash lamp with a pulse width of 1.2 ns at FWHM and a Philips XP-2020Q Photomultiplier tube were, respectively, used as the excitation source and for the fluorescence detection. Electrochemical measurements (cyclic voltammetry, CV) were made with a computer controlled EG&G PARC VersaStat Model 270 electrochemical instrument using a platinum disk working electrode as described elsewhere [15]. The solution was IR-compensated and the results were collected at 298 K. The following parameters and relations were used: scan rate (v), 50 mV s^{-1}; formal potential $E^\circ = 0.5(E_{pa} + E_{pc})$ where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; ΔE_p is the peak-to-peak separation. The potentials are referenced to a saturated calomel electrode (SCE) and are uncorrected for junction contributions.

2.3. Preparation of Schiff bases

The Schiff bases pfpd, pbpd, pfed and pbed were prepared following a reported [11a] procedure with a little modification.

2.3.1. N,N′-(bis(pyridin-2-yl)formylidene)-propane-1,3-diamine (pfpd) and N,N′-(bis(pyridin-2-yl)-benzylidene)propane-1,3-diamine (pbpd)

Propane-1,3-diamine (0.074 g, 1 mmol) and pyridine-2-carboxaldehyde (0.214 g, 2 mmol) were mixed together and refluxed in dehydrated alcohol (25 cm^3) for 10 h. The yellow solution that resulted was concentrated on a steam-bath and dried in vacuo over $CaCl_2$ to a yellow solid. Yield: 0.176 g (70%). pbpd was prepared (yield, 74%) using similar procedure except that 2-bezoylpyridine instead of pyridine-2-caboxaldehyde was used. *Anal.* Calc. for $C_{15}H_{16}N_4$ (pfpd): C, 71.4; H, 6.4; N, 22.2. Found: C, 72.0; H, 6.7; N, 22.5%. IR (KBr disc, cm^{-1}): ν(C=N) 1594. UV–Vis (MeCN): λ_{max}, 260 and 392 nm. Found: C, 80.4; H, 5.8; N, 14.2%. *Anal.* Calc. $C_{27}H_{24}N_4$ (pbpd): C, 80.2; H, 6.0; N, 13.9%. IR (KBr disc, cm^{-1}): ν(C=N) 1595. UV–Vis (MeCN): λ_{max}, 260 and 390 nm.

2.3.2. (N,N-diethyl,N′-(pyridin-2-yl)formylidene)-ethane-1,2-diamine (pfed) and (N,N-diethyl,N′-(pyridin-2-yl)benzylidene)-ethane-1,2-diamine (pbed)

The procedure is similar to the synthesis of pfpd/pbpd except that the reaction time is longer. *N*,*N*-diethylethane-1,2-diamine (0.116 g, 1 mmol) and pyridine-2-carboxaldehyde (0.107 g, 1 mmol) were refluxed in dehydrated alcohol (30 cm^3) for 12 h. The yellow solution was processed as above in case of pfpd to yield a semisolid, which was stored in vacuo over $CaCl_2$ for subsequent use. Yield: 0.153 g (75%). Pbed was prepared (yield, 78%) similarly using 2-benzoylpyridine instead of pyridine-2-carboxaldehyde. *Anal.* Calc. for $C_{12}H_{19}N_3$ (pfed): C, 70.2; H, 9.3; N, 20.4. Found: C, 70.4; H, 9.0; N, 20.7%. IR (KBr disc, cm^{-1}): ν(C=N) 1592. UV–Vis (MeCN): λ_{max}, 242 and 370 nm. Found: C, 76.3; H, 8.4; N, 14.6%. *Anal.* Calc. $C_{18}H_{23}N_3$ (pbed): C, 76.8; H, 8.3; N, 14.9%. IR (KBr disc, cm^{-1}): ν(C=N) 1590. UV–Vis (MeCN): λ_{max}, 245 and 372 nm.

2.4. Preparation of the complexes

Mononuclear type 1 complexes were prepared from both nitrate and perchlorate salts of cobalt(II) using 1:1:2 mole ratio of the metal salts, tetradentate blockers (pfpd and pbpd) and pseudohalides (azide, thiocyanate and cyanate). Type 2 compounds were isolated using a 1:1:3 ratio of the cobalt(II) salts, tridentate Schiff bases (pfed and pbed) and the pseudohalides. The typical syntheses with perchlorate salt are described below.

*2.4.1. [Co(pfpd)(N_3)$_2$] (**1a**) and [Co(pbpd)(N_3)$_2$] (**1b**)*

A methanolic solution (5 cm^3) of faint yellow pfpd (0.126 g, 1 mmol) was added dropwise to a pink $Co(ClO_4)_2 \cdot 6H_2O$ (0.183 g, 1 mmol) solution (5 cm^3) in the same solvent. To this NaN_3 (0.065 g, 2 mmol) in water (5 cm^3) was added slowly. The final red solution was filtered and left for slow evaporation in air at room temperature. After 3–4 days fine red microcrystalline product of **1a** separated out, which was filtered, washed with methanol and dried in vacuo over $CaCl_2$. Yield: 0.138 g (70%). Compound **1b** was prepared (yield, 72%) similarly except that pbpd instead of pfpd was used. *Anal.* Calc. for $C_{15}H_{16}N_{10}Co$ (**1a**): C, 45.58; H, 4.08; N, 35.43. Found: C, 45.72; H, 4.02; N, 35.65%. *Anal.* Calc. for $C_{27}H_{24}N_{10}Co$ (**1b**): C, 59.23; H, 4.42; N, 25.58. Found: C, 59.42; H, 4.45; N, 25.82%.

*2.4.2. [Co(pfpd)(NCS)$_2$] (**1c**) and [Co(pbpd)(NCS)$_2$] (**1d**)*

These were prepared (yield, 70–75%) using the same reaction condition and reaction stoichiometry as described in **1a**/**1b** except that NH_4NCS (2 mmol) in water (5 cm^3) instead of NaN_3 was added. The reaction solution was processed as above to result in crystalline **1c**/**1d**. *Anal.* Calc. for $C_{17}H_{16}N_6S_2Co$ (**1c**): C, 47.77; H, 3.77; N, 19.66. Found: C, 47.68; H, 4.72; N, 19.18%. *Anal.* Calc. for $C_{29}H_{24}N_6S_2Co$ (**1d**): C, 60.09; H, 4.17; N, 14.49. Found: C, 60.35; H, 4.22; N, 14.28.%.

*2.4.3. [Co(pfpd)(NCO)$_2$] (**1e**) and [Co(pbpd)(NCO)$_2$] (**1f**)*

These were also prepared (yield, 70–75%) using the same procedure as described in **1a**/**1b** except that NaNCO (2 mmol) in water (5 cm^3) instead of NaN_3 was added. *Anal.* Calc. for $C_{17}H_{16}N_6O_2Co$ (**1e**): C, 51.65; H, 4.08; N, 21.26. Found: C, 51.68; H, 4.10; N, 21.23%. *Anal.* Calc. for $C_{29}H_{24}N_6O_2Co$ (**1f**): C, 63.62; H, 4.42; N, 15.35. Found: C, 63.65; H, 4.40; N, 15.38%.

*2.4.4. [Co(pfed)(N_3)$_3$] (**2a**) and [Co(pbed)(N_3)$_3$] (**2b**)*

To a methanolic solution (5 cm^3) of $Co(ClO_4)_2 \cdot 6H_2O$ (0.183 g, 1 mmol) were added pfed (0.103 g, 1 mmol) in the same solvent (5 cm^3) and NaN_3 (0.098 g, 3 mmol) in water (5 cm^3). The deep wine red solution was filtered and was kept for slow evaporation. After 7 days **2a** was separated, washed with methanol and dried in vacuo over $CaCl_2$. Yield: 0.146 g (75%). Compound **2b** was prepared (yield, 72%) using a similar procedure as described above except that pbed instead of pfed was used. *Anal.* Calc. for $C_{12}H_{19}N_{12}Co$ (**2a**): C, 36.93; H, 4.91; N, 43.06. Found: C, 36.76; H, 3.84; N, 43.24%. *Anal.* Calc. for $C_{18}H_{23}N_{12}Co$ (**2b**): C, 46.35; H, 4.97; N, 36.04. Found: C, 46.27; H, 4.89; N, 36.22%.

*2.4.5. [Co(pfed)(NCS)$_3$] (**2c**) and [Co(pbed)(NCS)$_3$] (**2d**)*

These were prepared (yield, 70–72%) using the same reaction condition and reaction stoichiometry as described in **2a**/**2b** except that NH_4NCS (3 mmol) in water (5 cm^3) instead of NaN_3 was added. The reaction solution was processed as above to result in crystalline **2c**/**2d**. *Anal.* Calc. for $C_{15}H_{19}N_{12}S_3Co$ (**2c**): C, 34.48; H, 3.66; N, 32.17. Found: C, 34.60; H, 3.58; N, 32.10%. *Anal.* Calc. for $C_{21}H_{23}N_{12}S_3Co$ (**2d**): C, 42.13; H, 3.87; N, 28.08. Found: C, 42.25; H, 3.76; N, 28.25%.

2.4.6. *[Co(pfed)(NCO)$_3$] (2e) and [Co(pbed)(NCO)$_3$] (**2f**)*

These were also prepared (yield, 70–74%) using the same procedure as described in **2a**/**2b** except that NaNCO (3 mmol) in water (5 cm^3) instead of NaN_3 was added. *Anal.* Calc. for $C_{15}H_{19}N_{12}O_3Co$ (**2e**): C, 37.98; H, 4.04; N, 35.44. Found: C, 37.66; H, 4.07; N, 35.53%. *Anal.* Calc. for $C_{21}H_{23}N_{12}O_3Co$ (**2f**): C, 45.82; H, 4.21; N, 30.54. Found: C, 45.85; H, 4.01; N, 30.71%.

2.5. *X-ray crystallographic analysis*

Red single crystals of **1c** and dark brown crystals of **2b** suitable for X-ray analyses were obtained by slow evaporation of MeOH–H_2O (2:1) solutions of the reaction mixtures at room temperature (298 K). Diffraction data were measured at 293(2) K on a Siemens SMART CCD diffractometer equipped with a graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. The unit cell parameters were determined by least-squares method using all observed reflections. A summary of the crystallographic data and structure refinement parameters is given in Table 1. Of 12050 and 13562 collected reflections, 4378 and 4956 unique reflections were recorded using ω-scan technique for **1c** and **2b**, respectively. The intensity data were corrected for Lorentzian polarization effects and an empirical absorption correction based on ψ scans was employed [16]. The structures were solved by the heavy atom method using SHELXS-97 [17] and successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically and refined using a riding model. In the final difference Fourier map the residual maxima and minima for **1c** and **2b** were 0.268 and −0.241 and 0.501 and −0.346 e Å^{-3}, respectively. All calculations were carried out using SHELXL-97 [18].

3. Results and discussion

3.1. *Synthesis and formulation*

The hexacoordinated mononuclear complex [Co(pfpd)(NCS)$_2$] (**1c**) was initially formed in aqueous methanolic solution containing a 1:1:1 mixture of $Co(ClO_4)_2 \cdot 6H_2O$, pfpd and NH_4NCS – a reactant ratio expected to yield a dithiocyanato bridged dinuclear species of the composition [(pfpd)Co^{II}(NCS)$_2$Co^{II}(pfpd)](ClO_4)$_2$. However, microanalyses showed a 1:1:2 ratio of metal, blocking ligand and pseudohalide, and in the IR spectrum, no presence of perchlorate bands was noticed. Reactant ratio corresponding to the product stoichiometry afforded better yield of **1c**. An effort to get dinuclear

Table 1
Crystallographic data of [Co(pfpd)(NCS)$_2$] (**1c**) and [Co(pbed)(N_3)$_3$] (**2b**)

Complex	**1c**	**2b**
Empirical formula	$C_{17}H_{16}N_6S_2Co$	$C_{18}H_{23}N_{12}Co$
Formula weight	427.41	466.41
Colour	orange	dark brown
T (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	8.3095(5)	7.9753(6)
b (Å)	9.5110(6)	13.4972(11)
c (Å)	24.6886(16)	20.3435(16)
β (°)	98.2490(10)	99.789(2)
V (Å^3)	1931.0(2)	2158.0(3)
Z	4	4
D_{calc} (Mg m^{-3})	1.470	1.436
μ (mm^{-1})	1.118	0.828
F(000)	876	968
Crystal size (mm^3)	0.38 × 0.27 × 0.22	0.40 × 0.15 × 0.10
θ ranges (°)	2.30–27.51	1.82–27.54
$h/k/l$	−10,10/−12,12/−19,31	−9,10/−17,14/−26,16
Reflections collected	12050	13562
Independent reflections (R_{int})	4378 (0.0235)	4956 (0.0310)
Completeness to θ (°)	98.6	99.3
T_{max} and T_{min}	0.9486 and 0.7756	0.9486 and 0.6709
Data/restraints/parameters	4378/0/253	4956/0/282
Goodness-of-fit on F^2	0.788	0.745
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0308$, $wR_2 = 0.0578$	$R_1 = 0.0347$, $wR_2 = 0.0619$
R indices (all data)	$R_1 = 0.0647$, $wR_2 = 0.0634$	$R_1 = 0.0750$, $wR_2 = 0.0684$
Largest peak and hole (e Å^{-3})	0.268 and −0.241	0.501 and −0.346

species, in which the starting material was changed to $Co(NO_3)_2 \cdot 6H_2O$, and a 1:1:1 molar ratio of the nitrate salt, ligand and pseudohalide followed by addition of extraneous KPF_6 (2 equivalent) produced **1c** with lower yield. Use of a 1:1:2 molar ratio of nitrate salt, Schiff base and azide results in **1c** in good yield. The different syntheses are reproducible. Change of ligands from pfpd to pbpd and the pseudohalides from NCS^- to N_3^- and NCO^- showed similar behaviour and compounds $[Co(pfpd)(N_3)_2]$ (**1a**), $[Co(pbpd)(N_3)_2]$ (**1b**), $[Co(pbpd)(NCS)_2]$ (**1d**), $[Co(pfpd)(NCO)_2]$ (**1e**) and $[Co(pbpd)(NCO)_2]$ (**1f**) were isolated. Changing the tetradentate Schiff bases (L^1 = pfpd or pbpd) to tridentate Schiff bases (L^2 = pfed or pbed) and use of metal perchlorate, organic ligand and pseudohalide in 1:1:1.5 molar ratio – a reactant ratio expected to yield a triazido bridged dinuclear species of the composition $[(L^2)Co^{III}(N_3)_3Co^{III}(L^2)]ClO_4$, resulted mononuclear complexes of the type $[Co(L^2)(X)_3]$ (L = pfed, $X = N_3^-$, **2a**; NCS^-, **2b**; NCO^-, **2c**; L = pbed, $X = N_3^-$, **2d**; NCS^-, **2e**; NCO^-, **2f**). Microanalyses showed a 1:1:3 ratio of metal, blocking ligand and pseudohalide, and once again in the IR spectrum, no presence of perchlorate bands was noticed. Use of required molar ratios of the building units corresponding to formulation of the product afforded better yields of **2**. With a view to getting tribridged dinuclear species, the starting material was changed to $Co(NO_3)_2 \cdot 6H_2O$, and a 1:1:1.5 molar ratio of the nitrate salt, ligand and pseudohalide followed by addition of extraneous KPF_6 (1 equivalent). This also produced **2** but in lower yield. Use of a 1:1:3 molar ratio of nitrate salt, Schiff base and azide results in **2** in good yield. Once again all these syntheses are reproducible.

The complexes **1** and **2** are sufficiently stable in air and in the presence of moisture. Analytical data for all the complexes are consistent with the calculated values. The compounds are soluble in a range of common organic solvents like methanol, acetonitrile, dimethylformamide and dimethylsulphoxide but are insoluble in water. In MeCN they behave as non-electrolytes as are indicated [19] by their very low Λ_M (~5 Ω^{-1} cm^2 mol^{-1}) values. Room-temperature solid-phase magnetic susceptibility measurements show that type **1** complexes behave as three-electron paramagnets with μ_{eff} value ~3.9 BM whereas type **2** compounds are diamagnetic (singlet ground state with t_{2g}^6 configuration) (Table 2). In the IR spectra, the most striking observation in type **1** complexes is a sharp, single, intense band of the pseudohalides. Compounds **1a** and **1b** show the asymmetric stretch as a strong band at about 2030 cm^{-1}. Compounds **1c** and **1d** exhibit $\nu_{as}(CN)$ stretching vibration at about 2100 cm^{-1}. The position of the signal strongly suggests N-coordination of bound isothiocyanate [10]. Compounds **1e** and **1f** display asymmetric cyanate stretching vibration at about 2050 cm^{-1} which is substantially higher than the free ion value [20] and is consistent [21] with N-bonding rather O-bonding. The single band in each case is in line with the presence of *trans*-CoX_2 ($X = N_3^-$, NCS^-, NCO^-) frame in $[Co(L^1)(X)_2]$. Three distinct splittings (vide Table 2) of asymmetric stretching vibrations of the terminal pseudohalides in type **2** compounds are strongly suggestive of the less symmetric *meridional* structure over the more symmetric *facial* arrangement. The $\nu(C{=}N)$ stretching vibrations of the metal bound Schiff bases are seen at around 1590 cm^{-1}. Several bands in the range 2800–3000 cm^{-1} are assigned to the aliphatic $\nu(CH)$ stretching vibration of ligand. All other characteristic L vibrations are seen in the 1600–600 cm^{-1} range. X-ray structures of **1c** and **2b** show definite proof of this hypothesis.

The complexes exhibit several absorption bands in MeCN solutions in the 200–900 nm range. The high

Table 2
Some characterization data of the complexes

Compound	IR[a] (cm^{-1}) $\nu_{as}(X)$	UV–Vis[b] λ_{max}, nm (10^{-3} ε M^{-1} cm^{-1})	Λ_M[c] (Ω^{-1} cm^2 mol^{-1})	μ_{eff} (BM)	Co^{III}–Co^{II} E°_{298}, V (ΔE_p, mV)[e]
1a	2025	552 (0.55), 412 (0.73), 384 (12.76)	3	3.88	0.32 (70)
1b	2028	554 (0.54), 415 (0.70), 382 (12.98)	4	3.87	0.33 (70)
1c	2095	555 (0.52), 412 (0.72), 384 (12.78)	3	3.86	0.33 (70)
1d	2098	551 (0.55), 410 (0.75), 382 (13.01)	5	3.85	0.34 (70)
1e	2250	550 (0.56), 413 (0.71), 380 (13.12)	4	3.86	0.31 (70)
1f	2248	556 (0.52), 415 (0.69), 385 (12.68)	5	3.87	0.32 (70)
2a	2002, 2010, 2025	508 (0.68), 404 (0.74), 332 (16.82)	3	[d]	0.36 (70)
2b	2004, 2008, 2026	510 (0.66), 406 (0.71), 330 (16.71)	4	[d]	0.37 (70)
2c	2061, 2077, 2095	512 (0.64), 402 (0.76), 334 (16.23)	5	[d]	0.34 (70)
2d	2060, 2078, 2098	511 (0.63), 402 (0.75), 328 (17.08)	4	[d]	0.36 (70)
2e	2255, 2235, 2218	510 (0.65), 404 (0.73), 332 (16.79)	5	[d]	0.34 (70)
2f	2252, 2233, 2215	512 (0.63), 406 (0.70), 333 (16.74)	4	[d]	0.35 (70)

[a] KBr disc.

[b] In MeCN at 298 K.

[c] In MeCN at 298 K.

[d] Diamagnetic.

[e] Working electrode is platinum.

intensity band below 400 nm is of ligand origin assignable [11b] to intraligand n–π*/π–π* transition. Above this wavelength the transitions are LMCT for cobalt(III) complexes and MLCT type for cobalt(II) members as are evident from their intensity values (Table 2). The bands show systematic blue shift in going from type **1** to type **2** complexes. The spectral pattern supports [22] six-coordinate distorted octahedral symmetry around cobalt centre.

3.2. X-ray crystal structures

3.2.1. Crystal structure of [Co(pfpd)(NCS)$_2$] (**1c**)

An ORTEP view with atom numbering scheme of the mononuclear dithiocyanato complex, **1c**, is shown in Fig. 1. Selected bond lengths and angles relevant to the coordination sphere are listed in Table 3. The cobalt(II) centre is best described as a distorted octahedron with a CoN$_6$ chromophore. Distortion from the ideal octahedral geometry is due to the asymmetric nature of the bound tetradentate Schiff base and the deviations of the refine angles (90°/180°) formed at the metal centre (Table 3). The coordination includes two pyridine nitrogens [N(3), N(6)], two imine nitrogens [N(4), N(5)] of the Schiff base and two nitrogens [N(1), N(2)] of the terminal thiocyanates. The equatorial positions are occupied with the four nitrogen atoms [N(3), N(4), N(5) and N(6)] of the tetradentate ligand while the nitrogens [N(1), N(2)] of the isothiocyanato groups are placed at the axial positions. The degrees of distortion of the coordination sphere are reflected in the *cisoid* [77.11(7)–113.07(7)°] and the *transoid* angles [169.47(7)–174.59(7)°]. The equatorial Co–N distances are in the range [2.0982(17)–2.1695(18) Å], comparable to the corresponding values in similar systems [1–3]. Axial Co–N distances [2.0813(18)–2.0844(19) Å] indicate stronger coordination of the anionic isothiocyanate over neutral Schiff base. The *trans* N1–Co1–N2 angle has a value [174.59(7)°] close to the ideal 180.00°. The angles N(6)–Co(1)–N(5), N(5)–Co(1)–N(4) and N(4)–Co(1)–N(3) in the equatorial plane have values 77.40(7)°, 92.45(8)° and 77.11(7)°, respectively, which are much less than the N(3)–Co(1)–N(6) angle [113.07(7)°] where N(3) and N(6) belong to the two ends of the tetradentate Schiff base. Both isothiocyanates are almost linear with the same N–C–S angle 178.7(2)°. N–C [1.152(2)–1.160(2) Å] and C–S [1.618(2)–1.621(2) Å] bond lengths are as expected for N-coordination [12]. The bond lengths and angles pertaining the ligand network are close to expected values [9–11]. The propylenic part [N(5)–C(11)–C(10)–C(9)–N(4)] of the Schiff base is to some extent puckered. The sequestering of cobalt(II) by four hard N donor centres of the tetradentate chelator (pfpd) imparts hardness to the metal centre even in low oxidation state; this influences preferential N-coordination of both the terminal NCS$^-$ ions through electronegative hard N donor centres (Fig. 1) ignoring the other possibilities, viz., both S-coordination and N- plus S-coordinations.

Table 3
Selected bond lengths (Å) and bond angles (°) for [Co(pfpd)(NCS)$_2$] (**1c**)

Bond distances (Å)	
Co(1)–N(2)	2.0813(18)
Co(1)–N(1)	2.0844(19)
Co(1)–N(4)	2.0982(17)
Co(1)–N(5)	2.1061(18)
Co(1)–N(6)	2.1591(17)
Co(1)–N(3)	2.1695(18)
S(1)–C(1)	1.621(2)
S(2)–C(2)	1.618(2)
N(1)–C(1)	1.160(1)
N(2)–C(2)	1.152(2)
Bond angles (°)	
N(2)–Co(1)–N(1)	174.59(7)
N(2)–Co(1)–N(4)	93.73(7)
N(1)–Co(1)–N(4)	91.64(7)
N(2)–Co(1)–N(5)	89.91(7)
N(1)–Co(1)–N(5)	90.54(7)
N(4)–Co(1)–N(5)	92.45(8)
N(2)–Co(1)–N(6)	87.27(7)
N(1)–Co(1)–N(6)	87.56(7)
N(4)–Co(1)–N(6)	169.80(8)
N(5)–Co(1)–N(6)	77.40(7)
N(2)–Co(1)–N(3)	89.49(7)
N(1)–Co(1)–N(3)	91.05(7)
N(4)–Co(1)–N(3)	77.11(7)
N(5)–Co(1)–N(3)	169.47(7)
N(6)–Co(1)–N(3)	113.07(7)
C(1)–N(1)–Co(1)	156.96(19)
C(2)–N(2)–Co(1)	170.25(19)
N(1)–C(1)–S(1)	178.7(2)
N(2)–C(2)–S(2)	178.7(2)

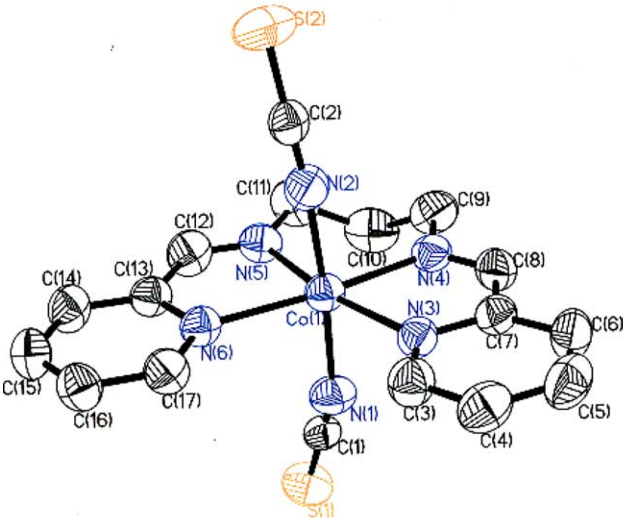

Fig. 1. ORTEP view of [Co(pfpd)(NCS)$_2$] (**1c**) with atom numbering scheme and 40% probability ellipsoids for all non-hydrogen atoms.

3.2.2. Crystal structure of [Co(pbed)(N_3)$_3$] (2b)

An ORTEP diagram of the mononuclear triazido compound **2b**, is displayed in Fig. 2. Selected bond lengths and angles pertaining to the coordination sphere are set in Table 4. The cobalt(III) centre adopts a distorted octahedral coordination sphere with a CoN_6 chromophore. Three nitrogen atoms [N(10), N(11), N(12)] of the tridentate Schiff base in combination with three nitrogen atoms [N(1), N(4), N(7)] of three different azides in a *meridional* alignment complete octahedral coordination of the metal ion. The equatorial positions are occupied by the three nitrogen atoms [N(10), N(11), N(12)] of the tridentate blocker and one nitrogen atom [N(4)] of the terminal azide while other two nitrogen atoms [N(1), N(7)] of the two azides are placed at the axial positions. Distortion from the ideal octahedral geometry is due to the asymmetric nature of the bound tridentate Schiff base and the deviations of the refine angles (90°/180°) formed at the metal centre (Table 4). The degrees of distortion from an ideal octahedral (90°) geometry are reflected in the *cisoid* [87.64(8)–96.69(8)°] and the *transoid* [167.90(7)–177.26(8)°] angles. Azide Co–N distances [1.9451(19)–1.9801(18) Å] indicate stronger coordination of the anionic terminals over those [1.8858(17)–2.0544(18) Å] of neutral Schiff base chelator. The azide terminals are almost linear with N–N–N angles 175.6(2)–177.7(2)°. N(1)–N(2) [1.185(2) Å], N(4)–N(5) [1.198(2) Å] and N(7)–N(8) [1.198(2) Å] distances are longer than the N(2)–N(3) [1.158(2) Å], N(5)–N(6) [1.150(3) Å] and N(8)–N(9) [1.160(2) Å] in usual manner [9–11] reflecting N(1), N(4) and N(7) connection of the pseudohalides. The ethylenic part [N(11)–C(13)–C(14)–N(10)] of the Schiff base is also to some extent puckered (Fig. 2) which has significant effect on variation of equatorial angles.

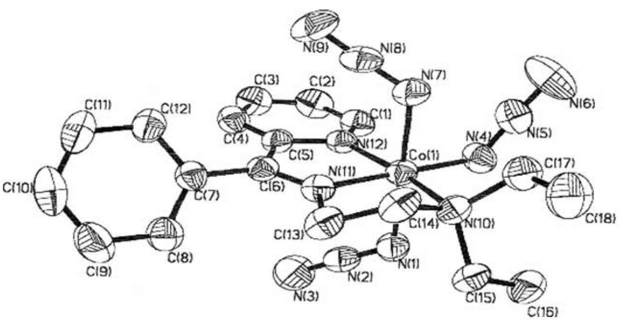

Fig. 2. ORTEP plot of [Co(pbed)(N_3)$_3$] (**2b**) with atom numbering scheme and 40% probability ellipsoids for all non-hydrogen atoms.

Table 4
Selected bond distances (Å) and bond angles (°) for [Co(pbed)(N_3)$_3$] (**2b**)

Bond distances (Å)	
Co(1)–N(1)	1.9801(18)
Co(1)–N(4)	1.9451(19)
Co(1)–N(7)	1.9637(19)
Co(1)–N(10)	2.0544(18)
Co(1)–N(11)	1.8858(17)
Co(1)–N(12)	1.9290(17)
N(1)–N(2)	1.185(2)
N(2)–N(3)	1.158(2)
N(4)–N(5)	1.198(2)
N(5)–N(6)	1.150(3)
N(7)–N(8)	1.198(2)
N(8)–N(9)	1.160(2)
Bond angles (°)	
N(2)–N(1)–Co(1)	119.14(15)
N(5)–N(4)–Co(1)	122.72(16)
N(8)–N(7)–Co(1)	120.11(16)
N(1)–Co(1)–N(10)	94.12(8)
N(4)–Co(1)–N(1)	87.64(8)
N(7)–Co(1)–N(1)	177.26(8)
N(12)–Co(1)–N(1)	88.29(8)
N(11)–Co(1)–N(1)	90.20(8)
N(4)–Co(1)–N(7)	90.67(9)
N(12)–Co(1)–N(10)	167.90(7)
N(4)–Co(1)–N(10)	96.69(8)
N(7)–Co(1)–N(10)	88.22(8)
N(3)–N(2)–N(1)	177.6(2)
N(6)–N(5)–N(4)	175.6(3)
N(9)–N(8)–N(7)	177.7(2)

3.3. Electrochemical properties

The electroactivity of the complexes was examined in MeCN solutions using cyclic voltammetry (CV) at a platinum-working electrode. A representative voltammogram is shown in Fig. 3. The complexes show (Table 2) nearly reversible (ΔE_p = 70–90 mV) oxidative response (for type **1**) and reductive response (for type **2**) presumably due to Co^{III}–Co^{II} couple as is shown in the following reactions:

$$[Co^{III}(L^1)(X)_2]^{1+} + e^- \rightleftharpoons [Co^{II}(L^1)(X)_2] \qquad (1)$$

$$[Co^{III}(L^2)(X)_3] + e^- \rightleftharpoons [Co^{II}(L^2)(X)_3]^{1-} \qquad (2)$$

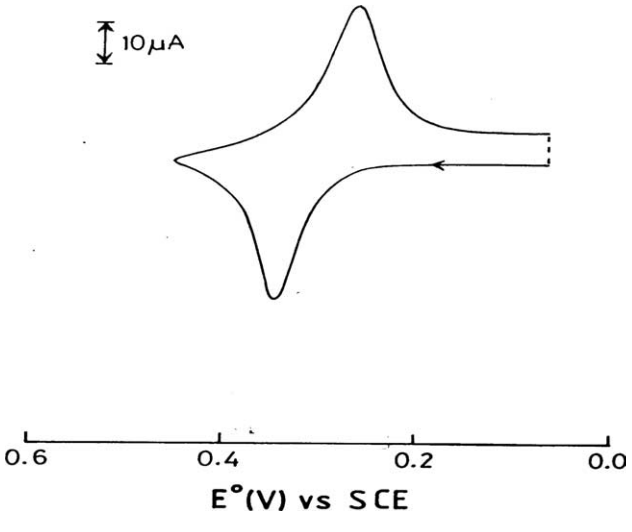

Fig. 3. Cyclic voltammogram of **2b** in MeCN at 298 K.

Table 5
Photophysical data for **1c** and **2b**

Compound	Emission (λ/nm)		Lifetime (ns)
	Fluorescence[a]	Phosphorescence[b]	
1c	478	550	2.33
2b	476	548	2.42

[a] In MeOH at room temperature (298 K).
[b] In MeOH at 77 K.

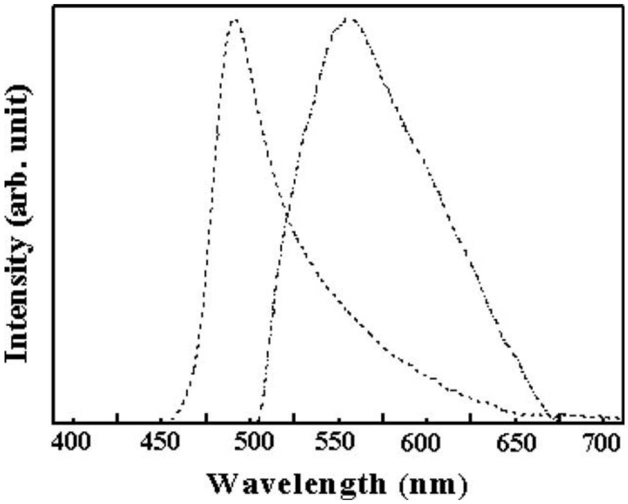

Fig. 4. Fluorescence (- - - - - -) in MeOH solution at 298 K, phosphorescence (·—·—·) in MeOH glass at 77 K of **1c**.

The responses are reproducible with no trace of decomposition after a number of cycles. The formal potentials lie close to ~0.3 V versus SCE. One-electron nature of the couple was verified with cobalt(II)azido complexes of arylazoimidazole ligands [23].

3.4. Luminescence properties

The spectroscopic data of selected complexes in methanol solutions and glasses are listed in Table 5. Compound **1c** shows emission at 478 nm while compound **2b** has a band at 476 nm at 298 K. These are assignable to intraligand $^1(\pi\text{–}\pi^*)$ fluorescence. A representative pattern is shown in Fig. 4. The lifetimes for **1c** and **2b** are 2.33 and 2.42 ns, respectively. In glassy solutions (77 K) a red shift is observable (550 nm for **1c** and 548 nm for **2b**) which is presumably due to $^3(\pi\text{–}\pi^*)$ phosphorescence [10].

4. Conclusion

We have prepared two different sets of cobalt(II) and cobalt(III) pseudohalide complexes by changing denticities of the Schiff base blockers. Structures of two representative complexes, $[Co(pfpd)(NCS)_2]$ (**1c**) and $[Co(pbed)(N_3)_3]$ (**2b**), are solved by X-ray study. Spectroscopic, electrochemical and other physicochemical properties strongly suggest that the structures **1a**, **1b** and **1d**–**1f** are cognate with **1c**, whereas **2a** and **2c**–**2f** with **2b**. The neutral tetradentate Schiff bases in combination with two monodentate pseudohalide ions satisfy hexacoordination of cobalt(II) as well as its charge; such a combination simultaneously satisfying both coordination number and charge of central ion results in stabilization of +2 oxidation state of the central. Similarly, judicious choice of one tridentate neutral Schiff base ligand and three pseudohalide ions satisfies hexacoordination of the central ion and its +3 oxidation level. This work shows that control of oxidation state of metal ion can be done through judicious choice of ligand matrices so as to satisfy coordination number and charge of metal ions simultaneously. The new complexes are good examples of luminous materials.

5. Supplementary data

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Centre Nos. 210735 for $[Co(pfpd)(NCS)_2]$ (**1c**) and 240924 for $[Co(pbed)(N_3)_3]$ (**2b**). Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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