DALTON
FULL PAPER

Low-spin octahedral cobalt(II) complexes of CoN_6 and CoN_4P_2 chromophores. Synthesis, spectroscopic characterisation and electron-transfer properties †

Bidyut Kumar Santra and Goutam Kumar Lahiri *

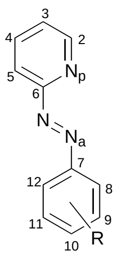
Department of Chemistry, Indian Institute of Technology, Bombay Powai, Mumbai-400076, India

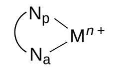
The reaction of 2-(arylazo)pyridines $(NC_5H_4)N{=}NC_6H_4R$ L^1–L^7 (R = H, *o*-Me/Cl, *m*-Me/Cl, *p*-Me/Cl) with cobalt(II) perchlorate hexahydrate in absolute ethanol under anaerobic conditions afforded low-spin $[Co^{II}L_3]^{2+}$ complexes, isolated as ClO_4^- salts. At room temperature the complexes are one-electron paramagnetic in nature, low-spin Co^{II}, $t_{2g}^6e_g^1$, $S = \frac{1}{2}$ and behave as 1 : 2 electrolytes in acetonitrile solvent. In acetonitrile solvent they show a ligand-to-metal charge-transfer (LMCT) band near 400 nm, an intraligand transition near 300 nm and ligand-field d–d transitions in the range 860–600 nm. The complexes exhibit quasi-reversible Co^{II}–Co^{III} couples near 1 V and six sequential ligand reductions (N=N groups) in the range 0.2 to −1.8 V *versus* saturated calomel electrode (SCE). At room temperature in the solid state they exhibit isotropic EPR spectra but at 77 K, both in the polycrystalline state and in the dichloromethane solution, display rhombic spectra. Reaction of $[Co^{II}L_3]^{2+}$ with 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) resulted in complete ligand-exchanged products with concomitant metal oxidation, low-spin $[Co^{III}(bpy)_3]^{3+}$ and low-spin $[Co^{III}(phen)_3]^{3+}$ respectively. The reaction of PPh_3 with the $[Co^{II}(L^7)_3]^{2+}$ [L^7 = 2-(*p*-chlorophenylazo)pyridine] yielded a partial ligand-exchanged product, low-spin $[Co^{II}(L^7)_2(PPh_3)_2]^{2+}$, isolated as its ClO_4^- salt. The complex is one-electron paramagnet and a 1 : 2 electrolyte in acetonitrile solvent. It displays an LMCT band at 401 nm, an intraligand transition at 305 nm and four d–d transitions in the range 870–640 nm. It exhibits irreversible Co^{II} to Co^{III} oxidation at 1.33 V (E_{pa}) and four successive ligand reductions in the range −0.30 to −1.1 V *versus* SCE. At 77 K the complex displays an axial EPR spectrum.

Cobalt(II) ion in octahedral complexes prefers to stabilise in high-spin configuration. Low-spin octahedral cobalt(II) species are rare.[1] Most of the available octahedral cobalt(II) complexes exist either in high-spin or in high-spin/low-spin equilibrium. Few authentic examples of spin-paired octahedral cobalt(II) species are known.[2]

The present work originates from our interest to develop octahedral tris complexes of cobalt(II) in low-spin state of the CoN_6 chromophoric class and to study their physicochemical properties. The other known $[Co^{II}(L{-}L)_3]$ chromophoric complexes stabilise Co^{II} either in high-spin state (*e.g.* L–L = 2,2′-bipyridine, 1,10-phenanthroline or ethane-1,2-diamine) or in high-spin/low-spin equilibrium [*e.g.* L–L = $CH_3N{=}C(CH_3)(CH_3)C{=}NCH_3$].[3,4] As a part of our programme we have chosen the 2-(arylazo)pyridine ligands, $(NC_5H_4)N{=}NC_6H_4R$ (L). Their interaction with metal ions has been explored extensively in recent times. The complexes have shown various fascinating metal- as well as ligand-based chemical and electrochemical properties, such as metal-ion-mediated thiolation and hydroxylation of the pendant phenyl ring of L,[5] metal-ion-assisted cleavage of the azo (N=N) bond,[6] isomerisation,[7] use as chemical and electrochemical oxidants,[8] oxo-transfer reaction,[9] catalysis and electrocatalysis.[8] The strong π-acidic property and asymmetric nature of the azopyridine ligands make them susceptible to chemical and electrochemical activities. Although the chemistry of many metal complexes of L have been emerged from the recent studies, those of cobalt have not been progressed so far. The richness of the ligating properties of 2-(arylazo)pyridine ligands has inspired us to study the hitherto unknown cobalt complexes and this study has led to the formation of very rare low-spin cobalt(II) tris chelates, $[Co^{II}L_3]^{2+}$.

To the best of our knowledge this work demonstrates the first authentic example of low-spin tris-octahedral cobalt(II) complexes of the CoN_6 chromophoric class. Herein we report the synthesis, spectroscopic, electron-transfer properties and reactivities of a group of low-spin $[Co^{II}L_3]^{2+}$ complexes.





ML

L^1 R = H
L^2 R = 8-Me
L^3 R = 8-Cl
L^4 R = 9-Me
L^5 R = 9-Cl
L^6 R = 10-Me
L^7 R = 10-Cl

Results and Discussion

Synthesis

Seven substituted 2-(arylazo)pyridine ligands used for the present study are abbreviated as L^1–L^7 respectively. The ligand L binds to the metal ions in a bidentate N_p, N_a manner forming a five-membered chelate ring, ML. The brown complexes $[Co^{II}L_3]^{2+}$ **1**–**7** have been synthesized by stirring $Co^{II}(ClO_4)_2\cdot 6H_2O$ and the appropriate L^1–L^7 in a stoichiometric 1 : 3 ratio in dry ethanol under a dinitrogen atmosphere, equation (1), and

$$Co^{II}(ClO)_4\cdot 6H_2O + 3L \xrightarrow[N_2]{\text{dry ethanol}} [Co^{II}L_3][ClO_4]_2\cdot H_2O \qquad (1)$$

isolated as monohydrated perchlorate salts. The use of absolute ethanol is essential to get the pure product in the solid state. If 95% ethanol is used only an impure gummy product is obtained

---

† *Non-SI units employed*: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, G = 10^{-4} T.

Table 1 Microanalytical,[a] magnetic moment,[b] conductivity[c] and IR[d] data

	Elemental analysis (%)					IR (cm^{-1})	
Compound	C	H	N	μ_{eff}/μ_B	Λ_M/Ω^{-1} cm^{-1} mol^{-1}	ν(N=N)	$\nu(ClO_4)$
1	48.11 (48.0)	3.46 (3.51)	15.18 (15.27)	1.98	280	1485	1104, 630
2	49.72 (49.83)	4.13 (4.04)	14.59 (14.53)	2.10	290	1455	1097, 630
3	42.55 (42.65)	2.76 (2.80)	13.68 (13.57)	2.12	300	1472	1111, 637
4	49.97 (49.83)	3.98 (4.04)	14.44 (14.53)	1.95	285	1453	1089, 624
5	42.73 (42.65)	2.84 (2.80)	13.69 (13.57)	1.99	297	1459	1094, 617
6	49.97 (49.83)	4.07 (4.04)	14.59 (14.53)	2.09	305	1479	1091, 637
7	42.53 (42.65)	2.82 (2.80)	13.64 (13.57)	2.13	302	1472	1088, 635
8	59.27 (59.19)	3.68 (3.78)	6.99 (6.90)	2.05	304	1448	1090, 620

[a] Calculated values are in parentheses. [b] In the solid state at 298 K. [c] In acetonitrile solution. [d] In KBr disc.

after removal of solvent *in vacuo*, which is difficult to purify. For the ligands L^1 and L^4 pure tris complexes separated directly from the reaction mixture, but for the other ligands (L^2, L^3, L^5–L^7) no solid mass precipitated directly. However, the addition of an excess of aqueous $NaClO_4$ to the above concentrated alcoholic solution resulted in an impure precipitate. Pure tris complexes **2**, **3** and **5**–**7** were obtained by washing the above solid several times with hexane.

The complexes can also be prepared starting from $CoCl_2\cdot 6H_2O$ in methanol. Here addition of an excess of aqueous $NaClO_4$ to the concentrated initial brown solution yielded an impure solid mass, from which the pure tris complexes can be obtained by thorough washing with hexane. All our attempts to prepare mixed-ligand complexes such as $[CoL_2Cl_2]$ by using different metal : ligand ratios have failed; in all the cases they ended up with the $[CoL_3]^{2+}$ tris complex. Although identical products can be obtained from both routes, the use of the first method appears to be more facile from the yield point of view.

The complexes are highly soluble in polar solvents such as acetonitrile, dimethylformamide (dmf) and dimethyl sulfoxide (dmso), moderately soluble in dichloromethane and chloroform and slightly soluble in benzene and water. The extent of solubility varies depending on the nature of the substituents present in the ligand framework. The microanalytical data (C, H, N) of the complexes listed in Table 1 are in good agreement with the calculated values, which confirms the gross composition of the tris chelates, $[CoL_3][ClO_4]_2\cdot H_2O$. The complexes are 1 : 2 electrolytes in acetonitrile solution (Table 1). Solid-state magnetic moment measurements at 298 K established that they are uniformly one-electron paramagnets (Table 1), *i.e.* they possess the low-spin $t_{2g}{}^6e_g{}^1$ ($S = \frac{1}{2}$) configuration. It is believed that the complexes have the sterically favourable meridional configuration (see later).

Infrared spectra

The Fourier-transform IR spectra of the complexes were recorded as KBr discs in the range 4000–400 cm^{-1}. Selected band positions are depicted in Table 1. A very strong and broad vibration near 1100 cm^{-1} and a strong and sharp vibration near 630 cm^{-1} are observed for all the complexes due to the presence of ionic perchlorate. A strong and sharp band near 1600 cm^{-1} is assigned to ν(C=C) + ν(C=N) stretchings. The ν(N=N) vibration is observed near 1450 cm^{-1} as a sharp peak. The stretching vibration of the water of crystallisation appears near 3400 cm^{-1} as a broad peak. The other expected vibrations are systematically present for all the complexes.

Table 2 Electronic spectral data in acetonitrile at 298 K

	λ/nm (ε/dm^3 mol^{-1} cm^{-1})					
Compound	d–d Transitions				Charge-transfer transitions	
1	862	776	702	650	392	318
	(322)	(447)	(456)	(429)	(18 356)	(37 140)
2	875	782	684	638	386	305
	(390)	(540)	(633)	(700)	(9820)	(39 700)
3	817	760	690	615	387	314
	(128)	(200)	(290)	(353)	(7020)	(39 650)
4	890	770	680	610	405	322
	(220)	(250)	(300)	(350)	(13 550)	(35 400)
5	880	782	696	592	385	318
	(205)	(284)	(442)	(700)	(10 100)	(50 300)
6	850	770	685	600	407	327
	(460)	(630)	(700)	(720)	(23 947)	(39 640)
7	840	760	678	612	398	324
	(200)	(280)	(300)	(340)	(14 370)	(36 200)
8	870	760	655	644	401	305
	(1335)	(1770)	(1640)	(1273)	(4450)	(8140)

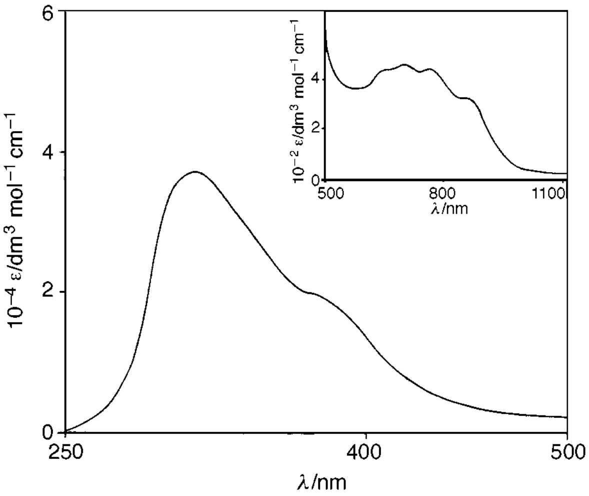


Fig. 1 Electronic spectrum of $[Co^{II}(L^1)_3][ClO_4]_2\cdot H_2O$ **1** in acetonitrile solvent. The inset shows low-energy d–d transitions

Electronic spectra

Solution electronic spectra of the complexes were recorded in acetonitrile solvent in the UV/VIS region (250–1100 nm). The data are listed in Table 2 and a representative spectrum is shown in Fig. 1. In the visible region the complexes exhibit one intense shoulder near 400 nm and a very intense sharp band near 300 nm. On the basis of their high intensities these two bands are assigned as charge transfer in nature. Since Co^{II} in the complexes is in the low-spin $t_{2g}{}^6e_g{}^1$ configuration, the band near 400 nm may be due to a ligand-to-metal charge-transfer transition.[10] The very intense band near 300 nm is presumably due to an intra-ligand π–π*/or n–π* transition.[5b] Here both bands are sensitive to the nature of the substituents present in the ligand framework. In the lower-energy part of the visible region all the complexes systematically display four weak transitions (Table 2). Based on the low intensities of these bands they are considered to be possible d–d transitions. In view of the molecular asymmetry in the meridional complexes **1**–**7**, the lifting of

Table 3 Electrochemical data at 298 K[a]

Compound	Co^{III}–Co^{II}, E°_{298}/V (ΔE_p/mV) Couple I	Ligand reductions, E°_{298}/V (ΔE_p/mV) II	III	IV	V	VI
1	1.09 (120)	0.12 (80)	−0.42 (80)	−0.84 (65)	−1.27 (100)	−1.64 (70)
2	0.95 (100)	0.00 (100)	−0.46 (80)	−0.90 (80)	−1.37 (90)	−1.80 (70)
3	1.13 (100)	0.22 (110)	−0.40 (100)	−0.83 (100)	−1.09 (100)	−1.39 (100)
4	1.03 (110)	0.11 (70)	−0.45 (80)	−0.86 (70)	−1.25 (90)	−1.67 (70)
5	1.36 (120)	0.215 (100)	−0.32 (90)	−0.68 (60)	−1.110 (90)	−1.43 (80)
6	0.99 (100)	0.03 (100)	−0.48 (80)	−0.88 (70)	−1.31 (80)	−1.73 (80)
7	1.20 (120)	0.19 (110)	−0.31 (60)	−0.69 (80)	−1.15 (100)	−1.47 (80)
8	1.33 (E_{pa})[b]	−0.33 (60)	−0.67 (60)	−1.07 (110)		

[a] Conditions: solvent, acetonitrile; supporting electrolyte, NEt_4ClO_4; reference electrode, SCE; solute concentration, 10^{-3} mol dm^{-3}, working electrode, platinum. Cyclic voltammetric data: scan rate, 50 mV s^{-1}; $E^{\circ}_{298} = 0.5\ (E_{pa} + E_{pc})$ where E_{pc} and E_{pa} are the cathodic and anodic peak potentials respectively. [b] Considered due to irreversible nature of the voltammogram.

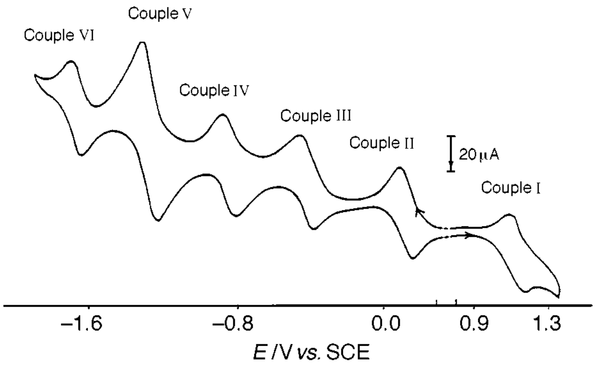


Fig. 2 Cyclic voltammograms (scan rate 50 mV s^{-1}) of a ≈10^{-3} mol dm^{-3} solution of complex **1** in acetonitrile at 298 K

orbital degeneracy of the states leads to a greater number of d–d transitions and some of them are actually distinctly resolved for all the complexes.[11] The intensities of the d–d bands are found to be high. This is possibly due to the influence of nearby intense charge-transfer transitions.

Electron-transfer properties

Electron-transfer properties of the complexes have been studied in acetonitrile solution by cyclic voltammetry (CV) using a platinum working electrode at 298 K. The complexes are electroactive with respect to the metal as well as ligand centres and display six reversible redox processes in the potential range ±2 V *versus* the saturated calomel electrode (SCE). Tetraethylammonium perchlorate was used as electrolyte. Representative voltammograms are shown in Fig. 2 and reduction potential data are in Table 3. The responses are quasi-reversible, the peak-to-peak separations of the couples lying in the range 70–120 mV. The assignments of the responses to the specific couples I–VI in Table 3 were made based on the following considerations.

The cobalt(III)–cobalt(II) couple. All the complexes display one quasi-reversible oxidative response near 1 V which is assigned to cobalt(II) to cobalt(III) oxidation, equation (2). The one-electron nature of the couple, equation (2), is confirmed by constant-potential coulometry. Although the yellow solution of $[CoL_3]^{3+}$ can be generated by coulometry, the oxidised solutions are unstable which has precluded the further characterisation of the oxidised trivalent $[Co^{III}L_3]^{3+}$ species. The formal potential of the couple [equation (2)] varies depending on the nature and the position of the substituents present in the ligand framework, *e.g.* the electron-donating Me group lowers the potential and the presence of the electron-withdrawing Cl^- makes the formal potential greater than for the unsubstituted ligand. The formal potential of the couple (2) follows the order **2** < **6** < **4** < **1** < **3** < **7** < **5** (Table 3).

$$[Co^{III}L_3]^{3+} + e^- \rightleftharpoons [Co^{II}L_3]^{2+} \qquad (2)$$

Under identical experimental conditions the oxidation of the $[Co(bpy)_3]^{2+}$ tris chelate (bpy = 2,2′-bipyridine) takes place at 0.2 V *versus* SCE, *i.e.* it is easily oxidisable to the cobalt(III) congener.[12] Thus the azopyridine ligand (L) can act as a much better stabiliser of cobalt(II) ion compared to the bpy ligand, which is of course due to the stronger π-acidic property of L.[13] This result is in accordance with the earlier observations on other metal complexes of L.[14]

Ligand reduction. The azopyridines (L) are well known electron-transfer centres. Thus each ligand can accommodate two electrons in one electrochemically accessible lowest unoccupied molecular orbital (LUMO) which is primarily azo in character.[15] Since the complexes contain three electroactive ligands, six successive reductions are therefore expected for each complex in principle. All the six expected reductions are actually observed in careful cyclic voltammetric experiments, equations (3)–(8). The reduction potentials data are listed in Table 3. The formal potential for the first reduction of L in cobalt complexes is uniformly more positive than that of free L, which is due to the positive charge of the metal ion. The observation of the complete set of six reductions in the tris chelate is rare. For $[Co(bpy)_3]^{2+}$ only four of the six are detected experimentally.[12]

$$[Co^{II}L_3]^{2+} + e^- \rightleftharpoons [Co^{II}L_2L^{\bullet -}]^{+} \qquad (3)$$

$$[Co^{II}L_2L^{\bullet -}]^{+} + e^- \rightleftharpoons [Co^{II}LL^{\bullet -}_2] \qquad (4)$$

$$[Co^{II}LL^{\bullet -}_2] + e^- \rightleftharpoons [Co^{II}L^{\bullet -}_3]^{-} \qquad (5)$$

$$[Co^{II}L^{\bullet -}_3]^{-} + e^- \rightleftharpoons [Co^{II}L^{\bullet -}_2L^{2\bullet -}]^{2-} \qquad (6)$$

$$[Co^{II}L^{\bullet -}_2L^{2\bullet -}]^{2-} + e^- \rightleftharpoons [Co^{II}L^{\bullet -}L^{2\bullet -}_2]^{3-} \qquad (7)$$

$$[Co^{II}L^{\bullet -}L^{2\bullet -}_2]^{3-} + e^- \rightleftharpoons [Co^{II}L^{2\bullet -}_3]^{4-} \qquad (8)$$

The one-electron nature of the first reduction [equation (3) and couple II in Fig. 2] is confirmed by constant-potential coulometry in acetonitrile solvent. The blue reduced solution is unstable, however we have managed to check the EPR spectrum by quickly freezing the reduced blue solution in liquid nitrogen (77 K). The starting $[Co^{II}L_3]^{2+}$ complexes are one-electron paramagnets and EPR active (see later) but the one-electron-reduced solutions are EPR silent. This indicates that the two unpaired electrons which are present in the reduced complexes $[Co^{II}L_2L^{\bullet -}]^{+}$ (one electron on the metal centre and the other on the ligand centre) are antiferromagnetically coupled. The extreme reactive nature of the other electrochemically reduced species did not allow us to study the reductions by spectroelectrochemical means. The one-electron nature of the other reductions [equations (4), (5) and (8); couples III, IV and VI in Fig. 2] is confirmed from current-height considerations. A direct comparison of the current height of couple V with those of the other couples suggests that V corresponds to a two-electron transfer and implies that the reductions corresponding to equations (6) and (7) have taken place simultaneously (see couple V, Fig. 2). Chemical reduction of the starting complex

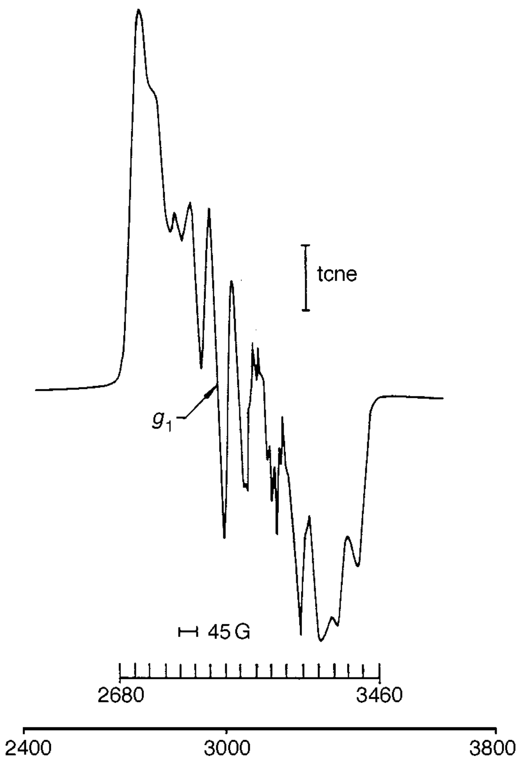


Fig. 3 X-Band EPR spectrum of complex **6** in dichloromethane solution at 77 K. The inner scale indicates the edge-to-edge linewidth of the spectrum; tcne = tetracyanoethylene

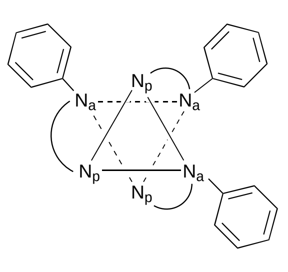
$[Co^{II}L_3]^{2+}$ by hydrazine hydrate in acetonitrile solvent also generated the same blue unstable reduced solution, which is also EPR silent.

Electron paramagnetic resonance spectra of $[CoL_3]^{2+}$ complexes

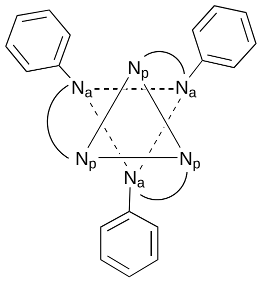
Consistent with the low-spin configuration, the $[CoL_3]^{2+}$ complexes displayed EPR spectra both in solid and solution states. A representative spectrum for one complex (**6**) is shown in Fig. 3. The EPR spectra in the solid state for one representative complex (**6**) and in solution for all the complexes have been studied. At both room and liquid-nitrogen temperature (77 K) in the polycrystalline state, complex **6** displays an EPR spectrum consistent with low molecular symmetry and hyperfine coupling to the ^{59}Co nucleus ($I = \frac{7}{2}$, 100% abundant). As the three components of the *g* tensor overlap severely we have been unable to assign the spectrum and hence derive either the *g* values or hyperfine couplings. Dichloromethane solutions of all complexes at 77 K display similar but better resolved spectra (Fig. 3). The 'crossing-point' (g_1 in Fig. 3) is found at $g = 2.117$ for **1**, 2.079 for **2**, 2.134 for **3**, 2.162 for **4**, 2.164 for **5**, 2.166 for **6** and 2.167 for **7**. Hyperfine coupling and the anisotropy of the *g* tensor leads to the signal being 618 G wide on average. There is also the possibility of superhyperfine coupling to N atoms of the ligands.

Isomer preference

Although the presence of asymmetric ligands in the $[CoL_3]^{2+}$ tris chelates allows the possibility of two geometrical isomers, meridional **A** and facial **B**, only one isomer has been consistently obtained experimentally for all the complexes. Since the spectral features of all complexes **1**–**7** are very akin, we therefore logically assume that they have the same isomeric structure. The paramagnetic nature of the complexes has prevented the identification of the specific geometry by NMR techniques. However, angular-overlap considerations strongly favour meridional geometry for the low-spin d^7, cobalt(II) case.[16]



A



B

Sterically the meridional geometry is generally more favoured. Similar ruthenium and iron tris chelates ($[RuL_3]^{2+}$, $[FeL_3]^{2+}$) have also been isolated in meridional form. Thus the collective considerations of angular-overlap, steric factors, spectral features and the earlier ruthenium and iron cases lead us to believe the existence of a meridional geometry for the present complexes.

Spin-state preference

Octahedral cobalt(II) complexes are known to prefer high-spin configuration. Low-spin cobalt(II) octahedral complexes can be expected only in the presence of a sufficiently strong ligand field ($\Delta_o \geqslant 15\,000$ cm^{-1}) which is required to get a ^{2}E ground state, originating from the ^{2}G state of the free ion.[1b] Owing to the non-availability of a sufficient number of ligand systems which can provide the minimum requirement of ligand-field strength, the low-spin configuration of Co^{II} in octahedral arrangement is rare. The ligand-field strength of (arylazo)pyridine ligands (L) makes them appropriate candidates to facilitate the preferential formation of unusual low-spin octahedral cobalt(II) complexes.

Reactions of $[CoL_3]^{2+}$ with other strong π-acidic ligands

(*a*) Complete ligand exchange with concomitant metal oxidation. Since unlike the azopyridine ligands (L) the other well known strong π-acidic ligands such as bipyridine and phenanthroline stabilise Co^{II} in the high-spin state in the respective tris chelates, it is therefore interesting to prepare mixed-ligand complexes comprising two such ligands of type $[Co^{II}L_{3-x}L'_x]^{2+}$ (L′ = bipyridine or phenanthroline, $x = 1$ or 2) to see the effect on magnetic and spectral features. Thus $[CoL_3]^{2+}$ was treated with bpy and phen in alcoholic solution but surprisingly the $[CoL_3]^{2+}$ complexes underwent complete ligand-exchange reaction and eventually yielded known low-spin $[Co^{III}(bpy)_3]^{3+}$ and $[Co^{III}(phen)_3]^{3+}$ complexes respectively.[3a]

The ligand L is believed to have a greater ligand-field strength compared to bpy and phen and that is why $[CoL_3]^{2+}$ complexes are stabilised in the low-spin state whereas the corresponding bpy and phen tris chelates are in the high-spin state. The driving force for the facile complete exchange of the strong π-acidic ligand L by the bpy and phen ligands is not clearly understood. The presence of cobalt(III) ion and the existence of a low-spin state in the tris-bpy and -phen complexes are understandable. A low Co^{II}–Co^{III} oxidation potential (≈0.2 V *versus* SCE) is the driving force to stabilise the metal ion in the trivalent state and the low-spin state is the preferred configuration for the cobalt(III) octahedral complexes.

(*b*) Partial ligand exchange without metal oxidation. The reaction of an excess of triphenylphosphine with $[CoL_3]^{2+}$ in methanol solvent resulted in green mixed-ligand complexes of type $[CoL_2(PPh_3)_2]^{2+}$, equation (9). Here one ligand L from the $[CoL_3]^{2+}$ has been exchanged by the two monodentate phosphine ligands and the exchange reaction has taken place without any change in metal oxidation state and spin configuration. Complex **8** has been isolated as its perchlorate salt. Although all the tris complexes **1**–**7** react similarly with PPh$_3$ and result in

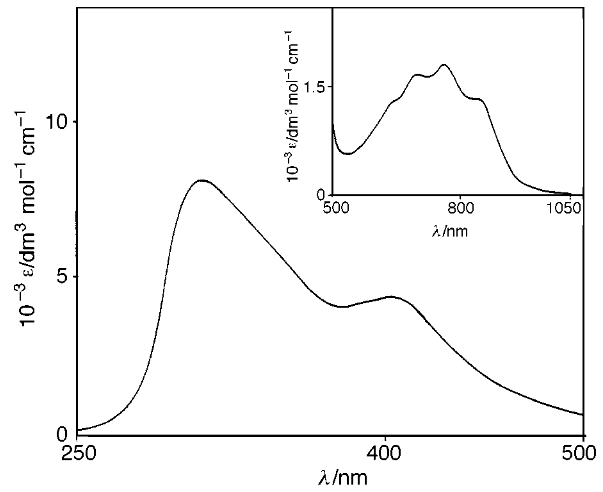
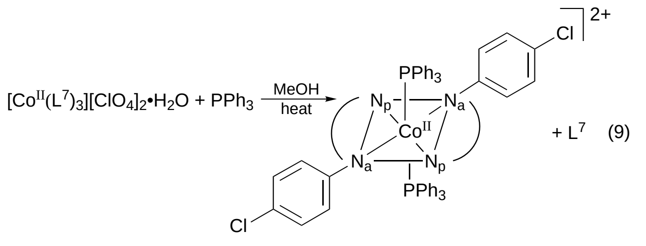


Fig. 4 Electronic spectrum of $[\mathrm{Co^{II}(L^7)_2(PPh_3)_2}][\mathrm{ClO_4}]_2$ **8** in acetonitrile solvent. The inset shows low-energy d–d transitions



(9)

8

similar green complexes a detailed study has been performed only for complex **7**.

Complex **8** is moderately soluble in non-polar solvents ($\mathrm{CH_2Cl_2}$, $\mathrm{CHCl_3}$, benzene) and highly soluble in polar solvents ($\mathrm{CH_3CN}$, dmf and dmso). In $\mathrm{CH_3CN}$ it is a 1 : 2 electrolyte. The one-electron paramagnetic nature of the complex has been established by solid-state magnetic moment measurement at 298 K (low-spin $\mathrm{Co^{II}}$, $S = \frac{1}{2}$). Microanalytical data (C, H, N) (Table 1) for the complex support the composition $[\mathrm{Co^{II}(L^7)_2(PPh_3)_2}][\mathrm{ClO_4}]_2$. The Fourier-transform IR spectrum displays perchlorate vibrations at 1090 and 620 $\mathrm{cm^{-1}}$ and phosphine vibrations at 720 and 510 $\mathrm{cm^{-1}}$. The azo (N=N) vibration appears at 1448 $\mathrm{cm^{-1}}$ (Table 1). All other expected vibrations due to ligand L are systematically present.

The ^{31}P NMR spectrum in $\mathrm{CDCl_3}$ exhibits one sharp signal at δ 29.2 which supports the *trans* configuration of the two $\mathrm{PPh_3}$ groups, as opposed to a *cis* arrangement. Such a configuration is expected from a steric point of view.[17]

In acetonitrile solvent complex **8** exhibits several bands in the UV/VIS region (250–1100 nm), Table 2, and the spectrum is shown in Fig. 4. The band at 401 nm is assigned to a ligand-to-metal charge-transfer transition and that at 305 nm is believed to be due to a ligand-based transition. In addition four more transitions have been observed in the lower energy part of the visible region (Table 2, Fig. 4) as for the starting $[\mathrm{Co^{II}L_3}]^{2+}$ complexes but here the bands are much more intense (Table 2). These four bands could be due to possible low-energy d–d transitions which might have originated from the lifting of orbital degeneracy of the states in the tetragonally distorted low-spin cobalt(II) complex. The relatively high intensity of the bands is not clearly understandable, however the influence of the tail of the nearby charge-transfer transitions may be responsible for this.

Electron-transfer properties of complex **8** have been studied in acetonitrile solvent using a platinum working electrode. Reduction potential values are given in Table 3 and the voltammograms are shown in Fig. 5. In acetonitrile solution the complex displays one irreversible oxidation process (anodic peak, E_{pa}) at 1.33 V *versus* SCE (couple I). No significant response on scan reversal in cyclic voltammetry is observed (Fig. 5). The oxidised complex thus decomposes rapidly on the cyclic voltammetric time-scale. This irreversible oxidative response is assigned to cobalt(II) to cobalt(III) oxidation [equation (10)]. Under identical experimental conditions the

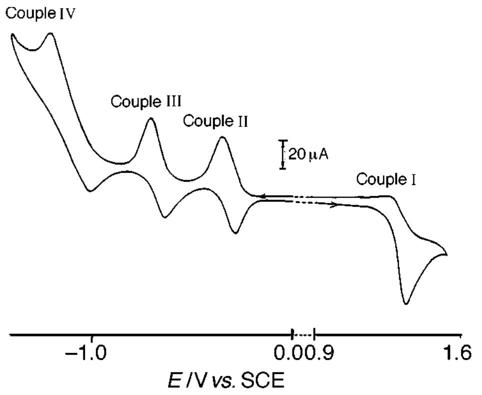


Fig. 5 Cyclic voltammograms (scan rate 50 mV $\mathrm{s^{-1}}$) of a ≈10^{-3} mol $\mathrm{dm^{-3}}$ solution of complex **8** in acetonitrile at 298 K

$$[\mathrm{Co^{II}(L^7)_2(PPh_3)_2}]^{2+} + e^- \longrightarrow [\mathrm{Co^{III}(L^7)_2(PPh_3)_2}]^{3+} \qquad (10)$$

E_{pa} of the cobalt(II)–cobalt(III) couple of the corresponding $[\mathrm{Co(L^7)_3}]^{2+}$ complex appears at 1.26 V. The observed 70 mV positive shift of the cobalt(II)–cobalt(III) oxidation potential on moving from complex **7** to **8** reveals that the (arylazo)pyridine ligand and phosphine together endow superior redox stability to cobalt(II).

Complex **8** contains two electroactive ligands L having one azo group in each, therefore four one-electron ligand-based reductions are expected, equations (11)–(14). Cyclic voltammograms of complex **8** exhibit three reversible reductions, couples II, III and IV (Fig. 5) at −0.33, −0.67 and −1.07 V (Table 3) *versus* SCE respectively. The one-electron nature of couples II and III and the two-electron stoichiometry of IV are established by cyclic voltammetric current-height considerations. Thus all the expected four ligand-based reductions are observed experimentally. Instead of getting all the four one-electron reductions separately, the first two [equations (11) and (12)] appear distinctly (couples II and III) and the other two [equations (13) and (14)] are overlapped at −1.07 V (Fig. 5, couple IV).

$$[\mathrm{Co^{II}(L^7)_2(PPh_3)_2}]^{2+} + e^- \rightleftharpoons [\mathrm{Co^{II}L^7(L^7)^{\bullet -}(PPh_3)_2}]^{+} \qquad (11)$$

$$[\mathrm{Co^{II}L^7(L^7)^{\bullet -}(PPh_3)_2}]^{+} + e^- \rightleftharpoons [\mathrm{Co^{II}(L^7)^{\bullet -}_2(PPh_3)_2}] \qquad (12)$$

$$[\mathrm{Co^{II}(L^7)^{\bullet -}_2(PPh_3)_2}] + e^- \rightleftharpoons [\mathrm{Co^{II}(L^7)^{\bullet -}(L^7)^{2\bullet -}(PPh_3)_2}]^{-} \qquad (13)$$

$$[\mathrm{Co^{II}(L^7)^{\bullet -}(L^7)^{2\bullet -}(PPh_3)_2}]^{-} + e^- \rightleftharpoons [\mathrm{Co^{II}(L^7)^{2\bullet -}_2(PPh_3)_2}]^{2-} \qquad (14)$$

The EPR spectrum of complex **8** was recorded in a chloroform–toluene (1 : 1) glass at 77 K. It is much simpler than those found for **1**–**7** and a tentative assignment is possible. The spectrum appears to be axial, consistent with the molecular symmetry for **8** assuming *trans*-$\mathrm{PPh_3}$ ligands. A hyperfine pattern can be discerned on the $g_{\parallel}$ component (see Fig. 6). The parameters derived from this assignment are $g_{\parallel} = 2.009$, $g_{\perp} = 2.003$, $A_{\parallel} = 6.78$ G. These values would be consistent with the unpaired electron residing in the $d_{x^2-y^2}$ orbital.

Conclusion

We have thus observed that (arylazo)pyridine ligands are appropriate candidates to stabilise the cobalt ion preferentially

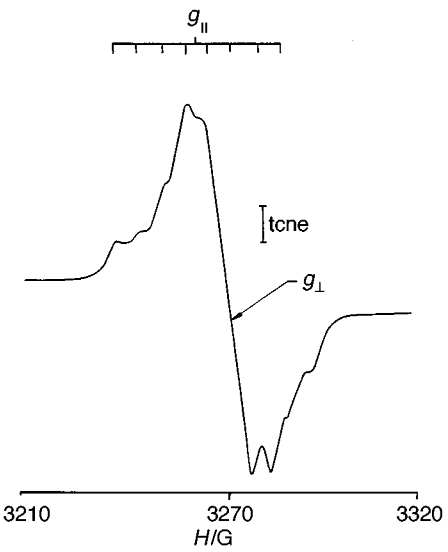


Fig. 6 X-Band EPR spectrum of complex **8** in a chloroform–toluene (1 : 1) glass at 77 K

in the bivalent state and can facilitate the formation of unusual low-spin cobalt(II) complexes in octahedral arrangement. The (arylazo)pyridines alone or in combination with a phosphine generate high-potential cobalt(II) tris chelate or mixed-ligand complexes. The complexes have shown sequentially a complete set of electron-transfer processes which are not often observable.

Experimental

Materials

Cobalt carbonate (Juhn Baker Inc. Colorado, USA) was converted into cobalt perchlorate by a standard method. Other chemicals and solvents were reagent grade and used as received. Silica gel (60–120 mesh) used for chromatography was of BDH quality. For spectroscopic/electrochemical studies HPLC grade solvents were used. Commercial tetraethylammonium bromide was converted into pure tetraethylammonium perchlorate by an available procedure.[18] Dinitrogen gas was purified by successive bubbling through alkaline dithionite and concentrated sulfuric acid.

Physical measurements

Solution electrical conductivity was checked using a Systronic conductivity bridge-305. Electronic spectra (1100–250 nm) were recorded using a Shimadzu-UV-160A spectrophotometer, FTIR spectra on a Nicolet spectrophotometer with samples prepared as KBr pellets. Magnetic susceptibility was checked with a PAR vibrating-sample magnetometer. The ^{31}P NMR spectra were obtained with a 300 MHz Varian Fourier-transform spectrometer. Cyclic voltammetry was carried out using a PAR model 362 scanning potentiostat electrochemistry system. A platinum-wire working electrode, a platinum-wire auxiliary electrode, and an aqueous saturated calomel reference electrode were used in a three-electrode configuration. A PAR model 279 digital coulometer was used for coulometry. The supporting electrolyte was NEt_4ClO_4 and the solute concentration was 10^{-3} mol dm^{-3}. The half-wave potential $E^{\ominus}_{298}$ was set equal to 0.5 ($E_{pa} + E_{pc}$), where E_{pa} and E_{pc} are the anodic and cathodic cyclic voltammetric peak potentials respectively. The scan rate used was 50 mV s^{-1}. All the experiments were carried out under a dinitrogen atmosphere. Electrochemical data were collected at 298 K and are uncorrected for the junction potential. The EPR measurements were made with a Varian model 109C E-line X-band spectrometer fitted with a quartz dewar for measurements at 77 K (liquid nitrogen). Spectra were calibrated by using tetracyanoethylene ($g = 2.0023$). The elemental analyses (C, H, N) were carried out with a Carlo Erba (Italy) elemental analyser.

Preparation of complexes

Compounds L^1–L^7 were synthesized by condensing 2-aminopyridine with the appropriate nitrosobenzene following the available procedure.[19] Complexes **1** and **4** were prepared by a general method, details are given for **1**.

Tris[2-(phenylazo)pyridine]cobalt(II) perchlorate monohydrate $[Co^{II}(L^1)_3][ClO_4]_2\cdot H_2O$ 1. 2-(Phenylazo)pyridine L^1 (1.0 g, 0.005 mol) was taken in absolute ethanol (10 cm^3) and stirred for 10 min under a dinitrogen atmosphere. Cobalt(II) perchlorate hexahydrate (0.65 g, 0.0017 mol) in absolute ethanol (10 cm^3) was added to the solution and the mixture was stirred for 5 h under a dinitrogen atmosphere. The brown precipitate thus obtained was filtered off and washed with absolute ethanol. The solid product was then dried under vacuum over P_4O_{10}. Yield 1.6 g (71%).

Complexes **2**, **3** and **5**–**7** were prepared by following the above procedure but no solid mass was obtained from the reaction mixture. Therefore the volume of the solution was reduced to 5 cm^3 under reduced pressure and an aqueous saturated solution of sodium perchlorate was added. The concentrated solution was kept in a refrigerator for 2 h. The brown precipitate thus obtained was filtered off and washed with a little (2 cm^3) ice-cold water and dried under vacuum over P_4O_{10}. The complexes were further purified by washing several times with *n*-hexane and dried *in vacuo* over P_4O_{10}. Yield 60–70%.

Bis[(2-*p*-chlorophenylazo)pyridine]bis(triphenylphosphine)-cobalt(II) perchlorate, $[Co^{II}(L^7)_2(PPh_3)_2][ClO_4]_2$ 8. To a methanolic solution (25 cm^3) of the complex $[Co(L^7)_3][ClO_4]_2\cdot H_2O$ **7** (0.2 g, 0.21 mmol) was added an excess of triphenylphosphine (0.17 g, 0.65 mmol). The mixture was heated to reflux for 6 h. The initial brown colour of **7** gradually changed to green. The progress of the reaction was monitored by TLC. The solvent was then evaporated to obtain a green gummy solid which was redissolved in acetonitrile (1 cm^3). An aqueous solution of saturated sodium perchlorate was added and the mixture was kept in a refrigerator overnight. The green solid thus obtained was filtered off, washed with diethyl ether and ice-cold water and dried *in vacuo* over P_4O_{10}. The dried product was dissolved in a small volume of chloroform and subjected to chromatography on a silica gel (60–120 mesh) column. With benzene as the eluent, the light yellow solution due to liberated L^7 separated first was rejected. Using a chloroform–acetonitrile (5 : 1) solution as eluent a green band separated. The green fraction was collected and evaporation of the solvents under reduced pressure yielded pure $[Co^{II}(L^7)_2(PPh_3)_2][ClO_4]_2$ **8**. The yield was 215 mg, 82%.

Acknowledgements

Financial support received from the Department of Science and Technology, New Delhi, India, is gratefully acknowledged. We are grateful to Professor A. Q. Contractor, Indian Institute of Technology (I.I.T.) Bombay, for providing the electrochemical instrumental facility. Special acknowledgement is made to Regional Sophisticated Instrumental centre, I.I.T. for providing NMR and EPR facilities. The suggestions of the reviewers at the revision stage were very helpful.

References

1 C. Ohrenberg, P. Ge, P. Schebler, C. G. Riordan, G. P. A. Yap and A. L. Rheingold, *Inorg. Chem.*, 1996, **35**, 749; F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 5th edn., 1988, p. 733; R. S. Drago, *Physical Methods for Chemists*, Saunders College Publishing, New York, 2nd edn., 1992, p. 448;

J. E. Huheey, E. A. Keiter and R. L. Keiter, *Inorganic Chemistry*, Harper Collins College Publishers, New York, 4th edn., 1993, p. 452.

2 W. N. Setzer, C. A. Ogle, C. S. Wilson and R. S. Glass, *Inorg. Chem.*, 1983, **22**, 266; J. R. Hartman, E. J. Hintsa and S. R. Cooper, *J. Chem. Soc.*, *Chem. Commun.*, 1984, 386; *J. Am. Chem. Soc.*, 1986, **108**, 1208; G. S. Wilson, D. D. Swanson and R. S. Glass, *Inorg. Chem.*, 1986, **25**, 3827; L. F. Warren and M. A. Bennett, *J. Am. Chem. Soc.*, 1974, **96**, 3340; R. C. Stoufer and D. H. Busch, *J. Am. Chem. Soc.*, 1956, **78**, 6016; Y. Nishida, K. Ida and S. Kida, *Inorg. Chim. Acta*, 1980, **38**, 113; V. Cuttica and M. Paoletti, *Gazz. Chim. Ital.*, 1922, **52**, 279; F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, 1957, **79**, 2733; 1958, **80**, 3578.

3 F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 1952, 3570; R. A. Palmer and M. C. L. Yang, *Chem. Phys. Lett.*, 1975, **31**, 492.

4 P. E. Figgins and D. H. Busch, *J. Am. Chem. Soc.*, 1960, **82**, 820.

5 B. K. Santra, G. A. Thakur, P. Ghosh, A. Pramanik and G. K. Lahiri, *Inorg. Chem.*, 1996, **35**, 3050; B. K. Santra and G. K. Lahiri, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 129; P. Bandyopadhyay, D. Bandyopadhyay, A. Chakravorty, F. A. Cotton, L. R. Falvello and S. Han, *J. Am. Chem. Soc.*, 1983, **105**, 6327.

6 G. K. Lahiri, S. Goswami, L. R. Falvello and A. Chakravorty, *Inorg. Chem.*, 1987, **26**, 3365.

7 R. A. Krause and K. Krause, *Inorg. Chem.*, 1980, **19**, 2600; S. Goswami, A. R. Chakravarty and A. Chakravorty, *Inorg. Chem.*, 1982, **21**, 2737; B. K. Ghosh, A. Mukhopadhyay, S. Goswami, S. Ray and A. Chakravorty, *Inorg. Chem.*, 1984, **23**, 4633; T. Bao, K. Krause and R. A. Krause, *Inorg. Chem.*, 1988, **27**, 759.

8 G. K. Lahiri, S. Bhattacharya, S. Goswami and A. Chakravorty, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 561.

9 S. Goswami, A. R. Chakravarty and A. Chakravorty, *J. Chem. Soc.*, *Chem. Commun.*, 1982, 1288.

10 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, New York, 1984, p. 724.

11 I. Bertini, G. Canti, C. Luchinat and A. Scozzafava, *J. Am. Chem. Soc.*, 1978, **100**, 4873.

12 N. Tanaka and Y. Sato, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 2059.

13 P. S. Rao, G. A. Thakur and G. K. Lahiri, *Indian J. Chem.*, *Sect. A*, 1996, **35**, 946.

14 S. Bhattacharya, *Polyhedron*, 1993, **12**, 235; S. Goswami, R. N. Mukherjee and A. Chakravorty, *Inorg. Chem.*, 1983, **22**, 2825.

15 N. Bag, A. Pramanik, G. K. Lahiri and A. Chakravorty, *Inorg. Chem.*, 1992, **31**, 40; B. K. Ghosh and A. Chakravorty, *Coord. Chem. Rev.*, 1989, **95**, 239.

16 J. K. Burdett, *Adv. Inorg. Chem. Radiochem.*, 1978, **21**, 113; *Inorg. Chem.*, 1976, **15**, 212; 1975, **14**, 375.

17 A. Pramanik, N. Bag, D. Ray, G. K. Lahiri and A. Chakravorty, *Inorg. Chem.*, 1991, **30**, 410; G. K. Lahiri, S. Bhattacharya, M. Mukherjee, A. K. Mukherjee and A. Chakravorty, *Inorg. Chem.*, 1987, **26**, 3359.

18 B. K. Santra, M. Menon, C. K. Pal and G. K. Lahiri, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 1387; D. T. Sawyer and J. L. Roberts, jun., *Experimental Electrochemistry for Chemists*, Wiley, New York, 1974, p. 167.

19 N. Campbell, A. W. Henderson and D. Taylor, *J. Chem. Soc.*, 1953, 1281.

Received 9*th September* 1997; *Paper* 7/06587F