Two New Quadridentate Schiff Base Complexes of Nickel(II) and Cobalt(III): Synthesis, Structure and Spectral Characterisation

Joy Chakraborty[a], Raj K. Bhubon Singh[b], Brajagopal Samanta[a],
Chirantan Roy Choudhury[a], Subrata K. Dey[a], Pritha Talukder[a], Manob J. Borah[b],
and Samiran Mitra[a]

[a] Department of Chemistry, Jadavpur University, Kolkata: 700 032, W.B., India
[b] Department of Chemistry, Nagaland University, Mokokchung 798601, Nagaland, India

Reprint requests to Prof. Samiran Mitra. Fax: 91-033-2414 6414. E-mail: smitra_2002@yahoo.com

Two novel quadridentate Schiff base complexes, $[Ni^{II}LH](ClO_4)_2 \cdot H_2O$ (**1**) and $[Co^{III}L]$-$(ClO_4)_2 \cdot H_2O$ (**2**) [LH, a Schiff base ligand: $Ph(OH)C(Me)=NCH_2CH_2N(CH_2CH_2NH_2)_2$] have been synthesised and characterised by elemental analyses, spectroscopic and electrochemical studies. The structures of both have been unequivocally established from single crystal X-ray diffraction studies. **1** and **2** crystallise in the monoclinic space group $P2_1/n$ having cell parameters $a = 8.536(1)$, $b = 13.832(4)$, $c = 18.194(2)$ Å, $\beta = 100.00(10)°$, $Z = 4$ for **1**, and $a = 10.819(5)$, $b = 14.301(2)$, $c = 14.224(1)$ Å, $\beta = 97.04(2)°$, $Z = 4$ for **2**. The complexes expose a square planar geometry around the metal centers chelated with three different types of nitrogen donor centers of the ligand.

Key words: Nickel(II)/Cobalt(III), Schiff Base Chelator, X-Ray Structure, Spectral Characterisation

Introduction

In recent years, an increasing effort has been dedicated to the preparation of mono- or dinuclear transition metal complexes containing chelating nitrogen ligands. Early and late transition metal complexes of this type have extensively been used as catalysts for a wide variety of reactions, including olefin polymerisation [1 – 3] and oxygen activation [4 – 7]. In this context, Schiff base complexes have a diverse range of applications in inorganic synthesis [8 – 11], as liquid crystals [12] and heterogeneous catalysts [13]. Nickel(II) and cobalt(III) complexes of multidentate Schiff base ligands have been extensively used [14 – 17] because such ligands can bind with one, two or more metals involving various coordination modes and allow the synthesis of homo- and/or heteronuclear metal complexes with interesting stereochemistry [18, 19]. The chemistry of nickel complexes with multidentate Schiff base ligands has attracted particular attention because this metal can exhibit several oxidation states [20] and such complexes have a strong role in bioinorganic chemistry and redox enzyme systems [21, 22] and may provide the basis of models for active sites of biological systems [23, 24] or act also as catalysts [25, 26]. Co(III) complexes derived from symmetrical and unsymmetrical Schiff bases have also drawn considerable attention in the past due to their important biological applications. Many model complexes of cobalt in both 2+ and 3+ oxidation states have been prepared and investigated. Ni(II) complexes with tetradentate N_2O_2 Schiff base ligands derived from salicylaldehyde have been studied, but complexes with tetradentate Schiff base ligands having an N_3O donor set are not that much frequent. Also, Co(III) complexes with uni-negative tetradentate Schiff base ligands have received less attention [27, 28]. It was shown that N_2O_2 ligand systems may act as tridentate as well as bidentate ligands in Cu(II) and Co(III) complexes [24, 29].

In continuation of these studies, we report herein the synthesis, characterisation, spectral studies and structural aspects of two metal complexes of Ni(II) and Co(III) with a quadridentate Schiff base ligand $Ph(OH)C(Me)=NCH_2CH_2N(CH_2CH_2NH_2)_2$. The structures have been confirmed by X-ray crystallography, which shows two square planar complexes of Ni(II) and Co(III) incorporating N_3O donor sets with an interesting feature of three different types of nitrogen donor centers in the same ligand.

Results and Discussion

The complexes were synthesised following the conventional literature method, *viz.* the reaction of ethano-

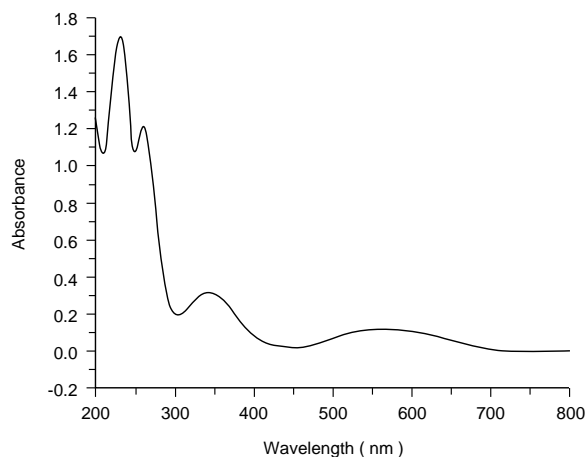Fig. 1. Room temperature UV/vis spectrum for **1**.
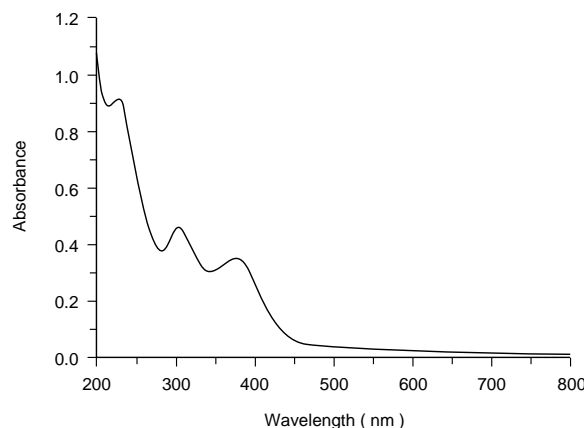
Fig. 2. Room temperature UV/vis spectrum for **2**.

lic solutions of nickel or cobalt salts with the Schiff base ligand under reflux condition.

Infrared spectra

The FT-IR spectra of **1** and **2** are fully consistent with the structural data obtained from X-ray diffraction studies. The broad absorption peaks for ν(O-H) appear at 3504 and 3448 cm^{-1} for **1** and **2** respectively, indicating the presence of lattice water molecules and phenolic O-H groups (for **1**), suggesting the coordination of the metal atom through the phenolic oxygen atom (without deprotonation). The strong absorption bands at 1586 and 1617 cm^{-1} for complexes **1** and **2**, respectively, may be assigned to the coordination of the nickel(II) and cobalt(III) ion by the azomethine (C=N) nitrogen atom [27, 30]. Strong absorption bands found at 626 and 680 cm^{-1} for **1** and **2**, respectively, may be due to ν[Ni-N(imino)] / ν[Co-N(imino)], and peaks at 374 and 364 cm^{-1} to ν(Ni-NH$_2$), at 362 and 355 cm^{-1} to ν(Co-NH$_2$) [31]. The bands in the region 1086 cm^{-1} for both complexes may be assigned to ν(C-O) stretching [30].

UV/vis spectra

Among the two complexes, **1** possesses a square planar geometry with diamagnetic nature that is reflected by the electronic spectrum (Fig. 1). It shows two absorption bands at 307 and 374 nm. The first one may be assigned to an LMCT transition, usually observed in metal Schiff base complexes containing phenolato ligands due to "phenolato-to-M" charge transfer, and the second one may be due to a $^{1}A_g \rightarrow {}^{1}E_g$ transition. Due to the strong metal ligand interaction,

the lowest energy state of Ni(II) becomes a singlet, resulting in a diamagnetic complex. Diamagnetism is a consequence of eight electrons being paired in the four low-lying d-orbitals (d_{xz}, d_{yz}, d_{z^2} and d_{xy}). The lower four orbitals are often so close together in energy that individual transitions from there to the upper $d_{x^2-y^2}$ orbital can not be clearly distinguished, resulting in a single absorption [32]. Two main bands, $^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ and $^{1}A_{1g} \rightarrow {}^{1}T_{2g}$, are normally observed in the d-d spectrum of Co(III) complexes. In the present case, we observed only the lower energy band at 554 nm (Fig. 2). The higher energy band was probably obscured by the ligand to metal charge transfer band [32].

Cyclic voltammetry

The electrochemical behavior of **1** has been investigated by cyclic voltammetry (Fig. 3) in acetonitrile solution (HPLC grade) under N$_2$ atmosphere to explore the extent of redox stabilisation of the Ni(II) state towards electrochemical oxidation. The CV scan of **1** in acetonitrile shows one irreversible Ni(III/II) couple at E$_{1/2}$ = 0.72 V *vs.* SCE with a ΔE_p value of 200 mV, which suggests that the Ni(III) species is unstable and undergoes rapid decomposition. The data obtained agrees well with those for a Ni(II) species.

In the cyclic voltammogram for the complex **2** (Fig. 4), one reductive response appears on the negative side of SCE at −0.71 V and is tentatively assigned to the reduction of the coordinated Schiff base ligand. Another irreversible reductive response found on the negative side of SCE (at −0.55 V) may be due to the reduction of the Co(III) centre.
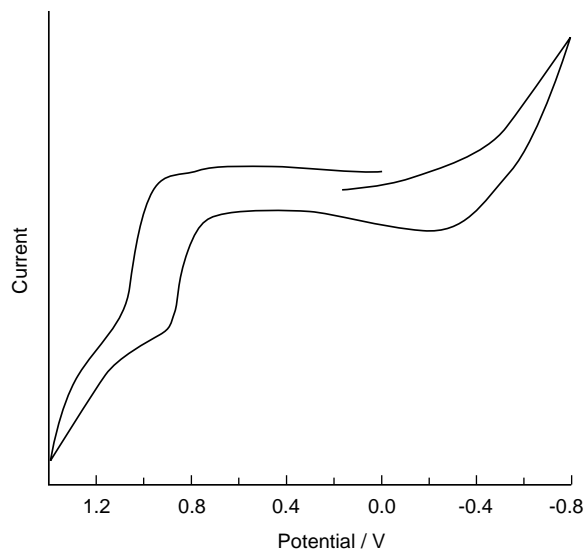
Fig. 3. Cyclic voltammogram for **1**.
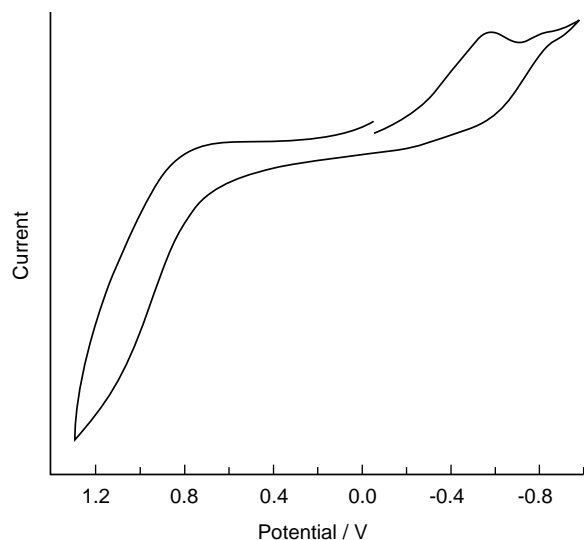
Fig. 4. Cyclic voltammogram for **2**.

Room temperature magnetic susceptibility studies

The effective magnetic moments at r. t. (300 K) for **1** and **2** are 0.001 and 0.013 B.M., respectively, which match well the spin-only values of nickel(II) and cobalt(III) ions in a square-planar environment.

X-ray crystal structures

The crystal structures of the complexes consist of discrete molecules held together by hydrogen bonds and van der Waal's interactions only. The ORTEP
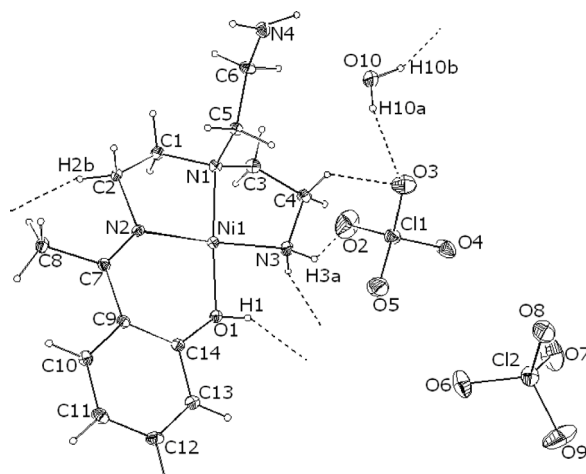
Fig. 5. ORTEP view of **1** showing intramolecular H-bondings (with 40% ellipsoid probability level for non-hydrogen atoms).
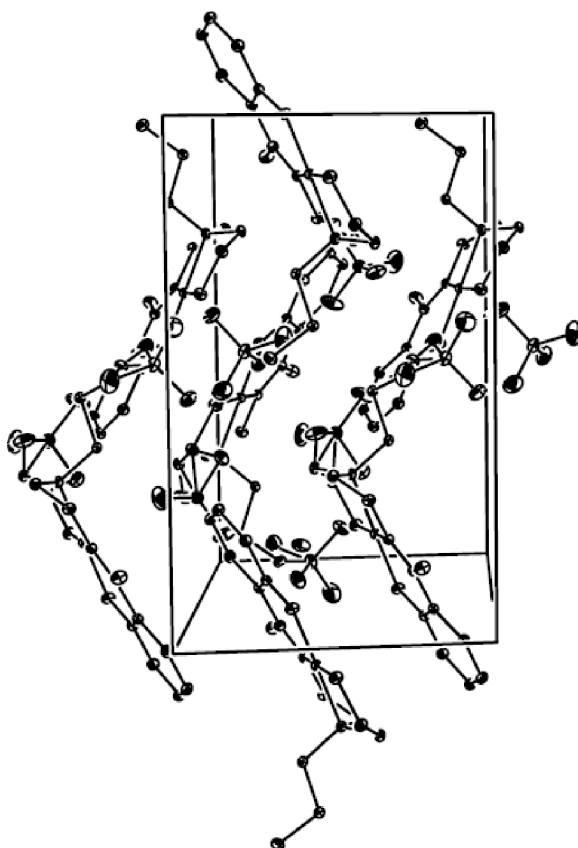
Fig. 6. Packing view of **1** in a direction normal to the (001) plane.

views and atom numbering schemes are shown in Figs. 5 and 7, respectively. The most important and
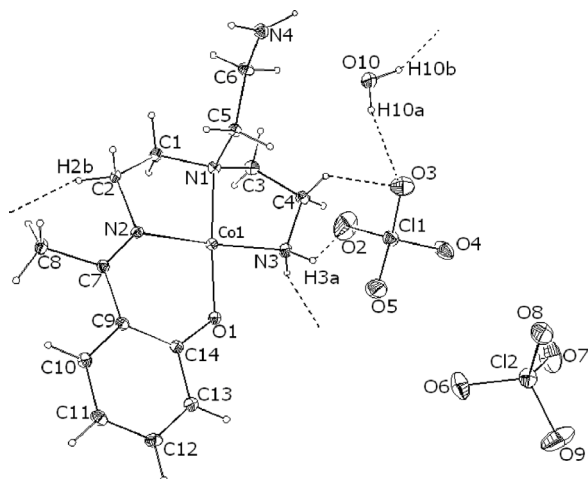
Fig. 7. ORTEP view of **2** showing intramolecular H-bondings (with 40% ellipsoid probability level for non-hydrogen atoms).

interesting feature of the ligand is that it has an N_3O donor set with three different types of nitrogen donor centers in a square planar geometry for both complexes around the metal centers. The nature of the ligand is strikingly different in the two complexes. In the case of complex **1**, the Schiff base is behaving as a neutral chelating ligand while in complex **2** it is an anionic chelating ligand due to the deprotonation of the phenolic OH group. So, in both cases two perchlorate anions are present in the lattice to give a charge balance to their dicationic complex counterparts. The square planes in the complexes suffer from a tetrahedral distortion as indicated by the deviations of the relevant atoms from the mean planes of the N_3O atoms. The distortions are quite large and significant, thereby reflecting the greater steric demand of the $-CH_2CH_2NH_2$ substituents on N(1) in both complexes. Angular distortion in the square plane is caused by different bite angles in the five and six membered chelate rings with the values O(1)-Ni(1)-N(2), 95.51(13)°; O(1)-Ni(1)-N(1), 176.12(13)°; N(2)-Ni(1)-N(1), 88.17(14)°; O(1)-Ni(1)-N(3), 90.03(15)°; N(2)-Ni(1)-N(3), 173.23(16)°; N(1)-Ni(1)-N(3), 86.39(16)° and O(1)–Co(1)–N(2), 95.5(7)°; O(1)–Co(1)–N(1), 172.4(7)°; N(1)–Co(1)–N(2), 86.6(7)°; N(1)–Co(1)–N(3), 85.2(8)°; N(2)–Co(1)–N(3), 166.8(8)°; O(1)–Co(1)–N(3), 94.0(7)° for **1** and **2**, respectively. The bond lengths Ni-N and Co-N are significantly different. For amino nitrogen atoms, *e. g.* N(3), they are longer [Ni(1)-N(3) 1.931(4) Å] than for imino nitrogen atoms N(2) [Ni(1)-N(2) 1.854(3) Å].
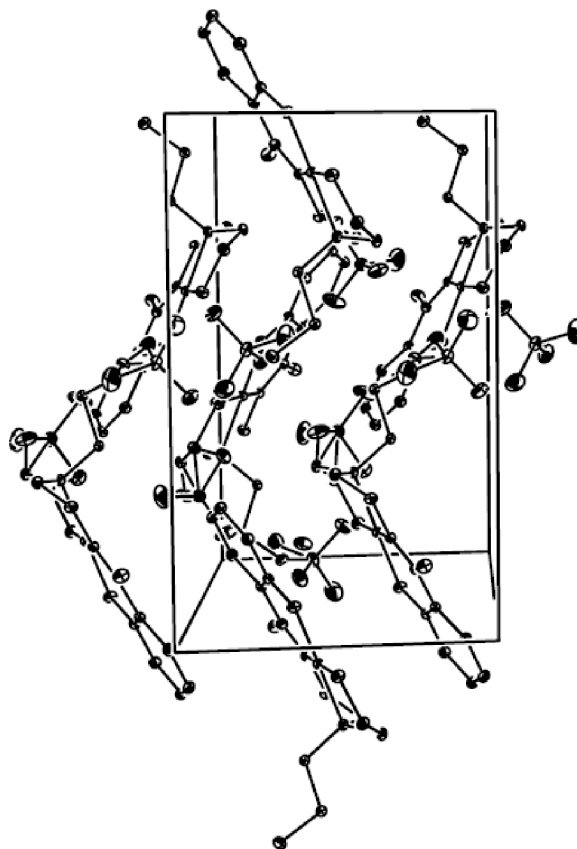

Fig. 8. Packing view of **2** in a direction normal to the (001) plane.

For tertiary amine nitrogen atoms N(1) the bond lengths are Ni(1)-N(1), 1.919(3) and Co(1)–N(1) 2.049(17) Å. Here, it may be noted that Ni-N and Co–N (amine) distances in the present square planar complexes are *ca.* 0.25 and *ca.* 0.37 Å shorter than Ni-N and Co–N distances found in a number of square planar Ni(II) and Co(III) complexes in the literature [22, 23], whereas the imino-N-metal distances Ni(1)-N(2) (1.854(3) Å) and Co–N(2) (1.944(18) Å) are nearly the same as reported earlier [16]. The unit N(1)-C(3)-C(4)-N(3) for **1** is puckered with a dihedral angle of *ca.* 24.3(4) ° and the unit N(1)-C(1)-C(2)-N(2) has a dihedral angle of *ca.* 39.7(4) °, whereas N(1)–C(1)–C(2)–N(2) and N(1)–C(3)–C(4)–N(3) for **2** have dihedral angles of *ca.* 52(3) and *ca.* 49(3) °, respectively. The Ni-O and Co-O bond lengths are slightly smaller than for similar square planar complexes reported earlier [22, 23] and seem to be correlated with the slightly longer C-O bonds C(14)-O(1) (1.320(5) Å).

Table 1. Selected bond lengths (Å) and bond angles (°) for **1** and **2**.

	Bond lengths	(Å)	Bond angles	(°)
1:	Ni(1)-O(1)	1.814(3)	O(1)-Ni(1)-N(1)	176.12(13)
	Ni(1)-N(1)	1.919(3)	O(1)-Ni(1)-N(3)	90.03(15)
	Ni(1)-N(3)	1.931(4)	N(2)-Ni(1)-N(3)	173.23(16)
	N(1)-C(1)	1.494(5)	C(5)-N(1)-Ni(1)	108.8(2)
	N(3)-C(4)	1.484(6)	C(3)-N(1)-Ni(1)	105.6(3)
	N(4)-C(6)	1.490(6)	C(7)-N(2)-Ni(1)	128.3(3)
	O(1)-C(14)	1.320(5)	C(4)-N(3)-Ni(1)	111.6(3)
	N(1)-C(5)	1.490(5)	O(1)-Ni(1)-N(2)	95.51(13)
	N(2)-C(2)	1.483(5)	N(2)-Ni(1)-N(1)	88.17(14)
	N(2)-C(7)	1.303(5)	N(1)-Ni(1)-N(3)	86.39(16)
	N(1)-C(3)	1.497(5)	C(1)-N(1)-Ni(1)	104.6(2)
	–	–	C(7)-N(2)-C(2)	118.9(3)
	–	–	C(2)-N(2)-Ni(1)	112.8(3)
2:	Co(1)-O(1)	1.858(14)	O(1)-Co(1)-N(1)	172.4(7)
	Co(1)-N(1)	2.049(17)	O(1)-Co(1)-N(2)	95.5(7)
	Co(1)-N(3)	2.01(2)	O(1)-Co(1)-N(3)	94.0(7)
	Co(1)-N(2)	1.944(18)	N(2)-Co(1)-N(1)	86.6(7)
	N(1)-C(1)	1.46(3)	N(2)-Co(1)-N(3)	166.8(8)
	N(3)-C(4)	1.47(3)	N(1)-Co(1)-N(3)	85.2(8)
	N(1)-C(3)	1.49(3)	C(5)-N(1)-Co(1)	110.6(12)
	–	–	C(1)-N(1)-Co(1)	100.0(13)
	–	–	C(3)-N(1)-Co(1)	103.9(13)
	–	–	C(2)-N(2)-Co(1)	112.0(14)
	–	–	C(7)-N(2)-Co(1)	126.8(15)
	–	–	C(4)-N(3)-Co(1)	110.7(15)

Table 2. Selected hydrogen bonding parameters.

D-H···A	d(D-H) Å	d(H···A) Å	d(D···A) Å	∠(DHA)°
1: N(3)-H(3A)···O(2)	0.82(5)	2.25(5)	2.843(7)	130(5)
O(10)-H(10A)···O(3)	0.82(5)	2.16(5)	2.963(6)	165(7)
C(2)-H(2B)···O(4)	0.91	2.56	3.061(6)	115
C(10)-H(10)···O(5)	0.97	2.55	3.431(7)	151
2: N(3)-H(3A)···O82	0.90(11)	1.28(15)	2.07(7)	143
O(10)-H(10B)···O(1)	0.8(3)	1.8(3)	2.63(3)	163
N(3)-H(3B)···O(9A)	0.9(3)	2.5(3)	3.36(8)	153

erature, especially for Co(III). Both complexes have been characterised by elemental analyses, spectroscopic and electrochemical investigations. Structures have been confirmed by single crystal X-ray diffraction studies.

Experimental Section

Materials

All the chemicals used for the synthesis were of analytical grade and purchased from Lancaster, UK. 2-Hydroxyacetophenone and tris(2-aminoethyl)amine were used as received without further purification. Nickel(II) perchlorate and cobalt(II) perchlorate were synthesised as described in the literature [33]. All solvents were freshly dried using standard methods.

Caution: Although no problems were encountered in this work, perchlorate salts in presence of organic materials are potentially explosive. Compounds should be prepared in small amounts and handled with care.

Physical techniques

The Fourier Transform Infrared Spectra (400 – 4000 cm^{-1}) of the complexes were recorded on a Perkin-Elmer Spectrum RX I FT-IR system with KBr discs. The UV/vis spectra were recorded at 20 °C on a Perkin-Elmer Lambda 40 UV/vis spectrometer using HPLC grade methanol as solvent with 1 cm quartz cuvettes. C, H, N analyses were carried out using a Perkin-Elmer 2400 II elemental analyser. Cyclic voltammetric measurements were performed using an EG&G PARC electrochemical analysis system (model 250-5-0) under a dry N$_2$ environment using conventional, three electrode configurations in purified acetonitrile (HPLC grade) with tetraethylammonium perchlorate as the supporting electrolyte. A planar EG&G PARC G0229 glassy carbon milli electrode was used as the working electrode at a scan rate of $v = 50$ mVs^{-1}. The Ni content was determined by the standard gravimetric estimation method using dimethylglyoxime. Magnetic susceptibilities were measured with a model 155 PAR vibrating sample magnetometer fitted with a Waker Scientific 175 FBAL magnet using Hg[Co(SCN)$_4$] as the standard.

The six membered rings are almost planar. Close scrutiny of the bond lengths in the ligand reveals a clear trend and this suggests that the N(2)-C(7) bonds (1.303(5) Å in **1**) retain their double bond character. The mode of H-bondings is more or less similar in both complexes (Table 2). The type is completely of intramolecular nature. These H-bondings are mainly distributed in between hydrogen atoms from the lattice water molecules or the ligand and the oxygen atoms of the ClO$_4$$^-$ anions. Presence of hydrogen bondings furnished by H-atoms at N or C atoms with perchlorate anions is clear from Fig. 5 and Fig. 7 corresponding to **1** and **2**. Packing views of the complexes **1** and **2** have been provided in Figs. 6 and 8, respectively. Relevant bond lengths and bond angles for **1** and **2** have been incorporated in Table 1. A few selected H-bonding parameters are given in the Table 2.

Conclusion

We have reported herein two novel transition metal complexes of Ni^{II} and Co^{III} prepared from a new Schiff base ligand incorporating a N$_3$O donor set. The most striking result is that the complexes are square planar with three different types of nitrogen donor centers in the same ligand which is not very common in the lit-

Table 3. Crystallographic data and structure refinements.

Parameters	1	2
Empirical Formula	$C_{14}H_{26}Cl_2N_4NiO_{10}$	$C_{14}H_{25}Cl_2CoN_4O_{10}$
M	540.00	539.21
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a [Å]	8.536(10)	10.819(5)
b [Å]	13.832(4)	14.301(2)
c [Å]	18.194(2)	14.224(1)
β [°]	100.00(10)	97.04(2)
V [Å^3]	2115.5(7)	2184(11)
Z	4	4
Temperature [K]	293(2)	293(2)
λ_{MoK_α} [Å]	0.71073	0.71073
Calculated density [g cm^{-3}]	1.695	1.640
μ [mm^{-1}]	1.230	1.089
$F(000)$	1120	1112
θ [°]	2.27 to 30.27	2.24 to 30.26
Index ranges	$0 \leq h \leq 12, 0 \leq k \leq 19, -25 \leq l \leq 25$	$0 \leq h \leq 15, 0 \leq k \leq 20, -20 \leq l \leq 20$
Total data	6697	6831
Unique data	6315	6523
R(int)	0.0235	0.0291
$I \geq 2\sigma(I)$	3708	3451
Data / restraints / parameters	6315 / 7 / 302	6523 / 584 / 384
Weighting scheme, w	$[\sigma^2(F_o^2) + (0.0663P)^2 + 1.9888P]^{-1}$	$[\sigma^2(F_o^2) + (0.0798P)^2 + 1.9099P]^{-1}$
Final R_1/wR_2 indices	0.0600 / 0.1333	0.0673 / 0.1522
Goodness-of-fit on F^2	1.03	1.02
R_1/wR_2 indices (all data)	0.1286 / 0.1645	0.1526 / 0.1897
Max. diff. peak and hole [e.Å^{-3}]	0.693 and -0.483	0.654 and -0.626

Syntheses

[C₆H₄(OH)C(CH₃)=NCH₂CH₂N (CH₂CH₂NH₂)₂]: Chelating Schiff base ligand (LH)

Tris(2-aminoethyl)amine (1.46 ml, 10 mmol) in 10 ml of ethanol was added to a solution of 2-hydroxyacetophenone (1.20 ml, 10 mmol) in 15 ml of ethanol. The solution was refluxed for 1.5 h and cooled to r. t. This solution was used without further purification.

[C₆H₄(OH)C(CH₃)=N(CH₂)₂N(CH₂CH₂NH₂)₂Ni(II)]-(ClO₄)₂·H₂O (1)

A solution of Ni(ClO₄)₂ · 6H₂O (330 mg, 1 mmol) in 15 ml absolute EtOH was added dropwise to a gently warmed 15 ml ethanolic solution of 1 mmol Schiff base ligand [1 : 1 molar ratio, M : L]. The solution was stirred for 3 h at 65 °C. The precipitated complex was then filtered and dissolved in a CH₂Cl₂ : CH₃CN = 2 : 1 v/v mixture. The resulting orange-red solution was filtered twice and the clear filtrate was kept for slow evaporation at r. t. Suitable orange platelet single crystals were collected by mechanical isolation after 15 d.

M. p. 125 °C. – UV/vis (CH₃OH): $\lambda_{max}(\lg \varepsilon) = 230$ nm (2.85). – IR (KBr disc): $\nu = 3504$ (O-H), 1586 (C=N), 1086 (C-O), 626 (Ni-N$_{imino}$), 374 and 364 (Ni-NH₂).

– C₁₄H₂₆Cl₂N₄NiO₁₀ (540.0): calcd. C 57.74, H 10.37, N 4.85, Ni 10.86; found C 57.77, H 10.38, N 4.89, Ni 10.82.

[(C₆H₄O)C(CH₃)=N(CH₂)₂N(CH₂CH₂NH₂)₂Co(III)]-(ClO₄)₂·H₂O (2)

The complex was synthesised following the same procedure as in the case of 1 except using Co(ClO₄)₂·6H₂O (365 mg, 1 mmol). The final brown solution was filtered twice and the filtrate was kept for slow evaporation at r. t. Suitable brown rod-shaped single crystals were collected by mechanical isolation after 3 d.

M. p. 135 °C. – UV/vis (CH₃OH): $\lambda_{max}(\lg \varepsilon) = 235$ nm (3.65). – IR (KBr disc): $\nu = 3448$ (O-H), 1617 (C=N), 1086 (C-O), 680 (Co-N$_{imino}$), 362, and 355 (Co-NH₂). – C₁₄H₂₅Cl₂N₄CoO₁₀ (539.21): calcd. C 57.93, H 10.41, N 4.67; found C 57.91, H 10.39, N 4.69.

X-ray crystallography

Cell dimension and intensity data were measured at 293 K from a good quality air stable orange platelet crystal of 1 (size 0.48 × 0.31 × 0.06 mm) and a brown rod shaped single crystal of 2 (size 0.44 × 0.08 × 0.06 mm), mounted on a fine-focus sealed tube of a FR590 Enraf Nonius Turbo CAD4 diffractometer equipped with a LiI scintillation detec-

tor and fitted with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) using non-profiled ω scans. Accurate cell parameters were obtained by least squares refinement with diffractometer angles for the entire data set for 25 reflections in the range of $9.2 < \theta < 14.4°$ and $8.9 < \theta < 13.7°$ for **1** and **2,** respectively. Measuring standard reflections at fixed intervals during the data collection checked the stability of the crystals. However, no significant loss of intensity was noted. Absorption corrections were carried out by using multiple and symmetry related measurements with the REFDELF program [34]. This absorption correction program consists of methods which have fallen out of favour in the recent past. It requires a refined model to provide a "correction" for the data based on the assumption that any consistent differences between the calculated and observed structure factors are due to absorption. When numerical corrections cannot be carried out, and if no extra intensities were measured, then these methods remain the only capable ones of providing some sort of correction for absorption. For most crystals containing elements heavier than the first row transition metals, it is likely that absorption is the most important contributor to the systematic errors. Both structures were solved by direct methods using the SIR-97 [35] program and refined by full-matrix least-squares on F^2 using all unique data for SHELXL-97 [36]. Partially occupied hydrogen atoms in the structure were obtained from the difference map, which were further included in the model. Details of crystal data, collection and refinement are listed in Table 3.

Supplementary material

X-ray crystallographic data in the CIF format corresponding to the complexes **1** and **2** have been deposited with the Cambridge Crystallographic Data Center (CCDC 296450, 296451). Supplementary crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

[1] C. M. Killian, D. J. Tempel, L. K. Johnson, M. Brookhart, J. Am. Chem. Soc. **118**, 11664 (1996).

[2] L. K. Johnson, C. M. Killian, M. Brookhart, J. Am. Chem. Soc. **117**, 6414 (1995).

[3] G. J. P. Britosek, V. C. Gibson, D. F. Wass, Angew. Chem., Int. Ed. Engl. **38**, 428 (1999) and references therein.

[4] B. Jung, K. D. Karlin, A. D. Zuberbuhler, J. Am. Chem. Soc. **118**, 3763 (1996) .

[5] V. Mahadevan, Z. Hou, A. P. Cole, D. E. Root, T. K. Lal, E. I. Solomon, T. D. P. Stack, J. Am. Chem. Soc. **119**, 11996 (1997) .

[6] P. L. Holland, K. R. Rodgers, W. B. Tolman, Angew. Chem., Int. Ed. Engl. **38**, 1139 (1999).

[7] S. J. Lange, H. Miyake, L. J. Que, J. Am. Chem. Soc. **121**, 6330 (1999).

[8] T. Katsuki, Coord. Chem. Rev. **140**, 109 (1995).

[9] Y. N. Ito, T. Katsuki, Bull. Chem. Soc. Jpn. **72**, 603 (1993).

[10] P. J. Pospisil, D. H. Carsten, E. N. Jacobsen, Chem. Eur. J. **2**, 974 (1996).

[11] T. Katsuki, J. Mol. Catal. A. **113**, 87 (1996).

[12] N. Hoshino, Coord. Chem. Rev. **174**, 77 (1998).

[13] L. Canali, D. C. Sherrington, Chem. Soc. Rev. **28**, 85 (1999).

[14] J. L. Sessler, J. W. Sibert, V. Lynch, Inorg. Chem. **29**, 4143 (1990).

[15] S. J. Brudenell, L. Spiccia, E. R. T. Tiekink, Inorg. Chem. **35**, 1974 (1996).

[16] a) K. Wieghardt, I. Tolksdorf, W. Herrmann, Inorg. Chem. **24**, 1230 (1985). b) D. H. Lee, N. N. Murthy, K. D. Karlin, Inorg. Chem. **35**, 804 (1996).

[17] J. L. Sessler, J. W. Sibert, V. Lynch, J. T. Markert, C. L. Wooten, Inorg. Chem. **32**, 621 (1993).

[18] Y. Ikawa, T. Nagata, K. Maruyama, Chem. Lett. 1049 (1993).

[19] T. Aono, H. Wada, Y. Aratake, N. Matsumoto, H. Ōkawa, Y. Matsuda, J. Chem. Soc., Dalton Trans. 25 (1996).

[20] A. Berkessel, M. Bolte, T. Nemann, L. Seidel, Chem. Ber. **129**, 1183 (1996).

[21] J. R. Lancaster, The Bioinorganic Chemistry of Nickel, VCH, New York (1998).

[22] A. F. Kolodziej, Prog. Inorg. Chem. **41**, 493 (1994).

[23] R. K. Parashar, R. C. Sharma, A. Kumar, G. Mohan, Inorg. Chim. Acta **151**, 201 (1998).

[24] D. X. West, H. Gebremedhin, R. J. Butcher, J. P. Jasinki, A. E. Liberta, Polyhedron **12**, 2489 (1993).

[25] E. Fujita, B. S. Brunschwig, J. Ogata, S. Yanagida, Coord. Chem. Rev. **132**, 195 (1994).

[26] E. Kimura, S. Wada, M. Shionoya, Y. Okazaki, Inorg. Chem. **33**, 770 (1994).

[27] N. Mondal, D. K. Dey, S. Mitra, K. M. A. Malik, Polyhedron **29**, 2707 (2000).

[28] J. P. Costes, F. Dahan, J. M. Domimguez-Vera, J. P.

Laurent, J. Ruiz, J. Sotiropoulos, Inorg. Chem. **33**, 3908 (1994).

[29] K. Yamanouchi, S. Yamada, Inorg. Chim. Acta **12**, 109 (1975).

[30] N. Mondal, S. Mitra, V. Gramlich, S. Ozra Ghodsi Mahalli, K. M. A. Malik, Polyhedron **20**, 135 (2001).

[31] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B: Applications in Coordination, Organometallic and Bioinorganic Chemistry, 5th Edition, Wiley, New York (1997).

[32] a) A. B. P. Lever, Inorganic Electronic Spectroscopy, 2nd Edn., Elsevier Science, New York (1984); b) D. N. Sathanarayan, Electronic Absorption Spectroscopy and Related Techniques, p. 257, University Press, Oxford, UK (2001).

[33] K. M. A. Malik, S. Mitra, R. K. Bhubon Singh, J. Chem. Crystallogr. **29**, 877 (1999).

[34] N. Walker, D. Stuart, Acta Crystallogr. **A39**, 158 (1983).

[35] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. **32**, 115 (1998).

[36] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement; Universität Göttingen: Göttingen, Germany (1997).