

Circular Dichroism Spectra of Mononuclear Complexes of Fe(II), Co(II) and Ni(II) with a chiral Schiff base R-1,2-propane bis(5-imino-1-phenyl-1,3-hexadione)

NASIR AHMAD, SHEHNAZ IQBAL AND ROSHAN AHMAD
Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan

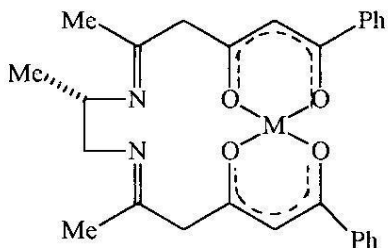
(Received 11th March, 1997, revised 17th August, 1997)

Summary: The CD and absorption spectra of mononuclear $[\text{Co}(\text{R-pn}(\text{BAA})_2)]$, $[\text{Ni}(\text{R-pn}(\text{BAA})_2)] \cdot \text{H}_2\text{O}$ and $[\text{Fe}(\text{R-pn}(\text{BAA})_2)]$ in three solvents i.e. Acetonitrile, chloroform and dioxane are reported. The CD of these complexes is influenced by the solvent. These studies indicate that metal ion in $[\text{Fe}(\text{R-pn}(\text{BAA})_2)]$ shifts from $\text{O}_2\text{-O}_2$ to $\text{N}_2\text{-O}_2$ compartment of the ligand in acetonitrile and dioxane solutions while in chloroform solution it is predominantly bonded to $\text{O}_2\text{-O}_2$ part. The CD bands of these complexes are interpreted in terms of electronic excitations to unidimensional levels. Further, Δ absolute configuration around the metal ions is assigned to these complexes.

Introduction

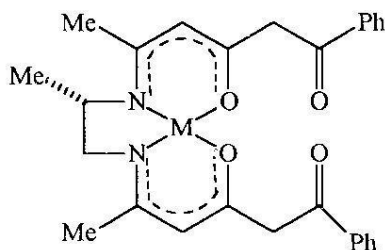
The synthesis, characterization and antibacterial properties of complexes of bivalent metal ions, VO(IV), Fe(II), Co(II), Ni(II), Cu(II) and UO₂(VI) with a chiral Schiff base, R-1,2-propane bis[5-imino-1-phenyl-1,3-hexadione), (R-1,2-pn(HBAA)₂) have been reported earlier [1]. It was observed that in solid state, VO(IV), Fe(II), Cu(II) and UO₂ (VI), occupied $\text{O}_2\text{-O}_2$ compartment (I) while Co(II) and Ni(II) were bonded to $\text{N}_2\text{-O}_2$ part of the ligand (II).

The circular dichroism (CD) spectra of $\text{O}_2\text{-O}_2$ bonded $[\text{VO}(\text{R-pn}(\text{BAA})_2)]$, $[\text{Cu}(\text{R-pn}(\text{BAA})_2)]$ and $[\text{UO}_2(\text{R-pn}(\text{BAA})_2)\text{C}_3\text{H}_7\text{O}]$ measured in chloroform, acetonitrile and dioxane solutions has also been reported from our laboratory [2]. As there are two adjacent and dissimilar compartments available for coordination in this ligand, complexes of either type are expected to exhibit different spectral and chemical properties. As CD is more sensitive to changes in molecular framework, it is considered



M = VO(V), Fe(II), Cu(II), UO₂(VI)

(I)



M = Co(II), Ni(II)

(II)

appropriate to investigate and compare the spectra of O₂-O₂ and N₂-O₂ bonded complexes of R-pn(HBAA)₂.

In this paper, CD spectra of N₂-O₂ bonded mononuclear complexes, [Co(R-pn(BAA)₂)] and [Ni(R-pn(BAA)₂)]·H₂O, in three solvents i.e. acetonitrile, chloroform and dioxane are reported. Although the metal ion in solid [Fe(R-pn(BAA)₂)] is bound in O₂-O₂ compartment, its solution CD spectra is representative of N₂-O₂ bonded species and is also discussed in this communication. The CD spectra of these species are influenced by solvents. Further, CD bands are assigned to electronic transitions within *d* orbitals.

Results and Discussion

The CD spectra of three mononuclear complexes, [Co(R-pn(BAA)₂)], [Ni(R-pn(BAA)₂)] and [Fe(R-pn(BAA)₂)] were studied in acetonitrile (CH₃CN), chloroform (CHCl₃) and dioxane (C₄H₈O₂) solutions. These spectra are reproduced in Fig. 1-3 and data on CD band positions alongwith absorption bands is given in Table-1.

The absorption spectra of these complexes in chloroform solution consist of 1-2 bands between 22,727-30,303 cm⁻¹ with molar absorptivity values of 4.63-11.47 × 10³ M⁻¹ cm⁻¹. The ligand has an intense band at 25,088 cm⁻¹ due to azomethine chromophore which shifts to 24,390-25,974 cm⁻¹ in complexes. The absorption spectrum of [Ni(R-pn(BAA)₂)]·H₂O has a shoulder band at 28,727 cm⁻¹ and a very

intense band at 22,604 cm⁻¹. These intense bands arise from allowed MLCT transitions.

In the crystal field region, two absorption bands at 17,094 cm⁻¹ (ε 30 M⁻¹ cm⁻¹) and 16,129 cm⁻¹ (ε 290 M⁻¹ cm⁻¹) were observed for [Fe(R-pn(BAA)₂)]. These bands seem to arise from ¹A₂ → ¹A₂ transition in a low spin, distorted octahedral species. The crystal field bands in [Co(R-pn(BAA)₂)] and [Ni(R-pn(BAA)₂)]·H₂O are masked by the very strong charge transfer bands which spread over a wide range of the spectrum.

The CD of [Co(R-pn(BAA)₂)] (Fig. 1) in three solvents consist of oppositely signed couplet of bands between 24,510-24,631 cm⁻¹ and 28,169-28,571 cm⁻¹ due to azomethine chromophore while a positive Cotton band between 18,182-692 cm⁻¹ in the crystal field region is observed. All of these bands are shifted to lower frequency (red shift) as solvents are changed from CH₃CN > CHCl₃ > C₄H₈O₂ and indicate weaker solute-solvent interaction in the same order. The very strong negative component of azomethine couplet lie on the lower frequency side in this case. The familiar couplet of bands may be originated from MLCT between metal and azomethine moiety of the ligand. The weak positive Cotton band between, 18,182-18,682 cm⁻¹ may be assigned to a spin allowed electronic transition to ⁴B₁ upper level of this tetragonally distorted complex. Similar band assignments have been reported for a number of complexes of chiral antibiotics formed in solution e.g. [Co((+)-CCS)₃]ⁿ⁺ 19,231 cm⁻¹, [Co((+)-

Table-1: Absorption and Circular Dichroism Spectra of Mononuclear Complexes of R-pn(HBAA)₂ in different solvents.

	Circular Dichroism Spectra in								Band Assignment
	Absorption in CHCl ₃		Acetonitrile		Chloroform		Dioxane		
	ν (cm ⁻¹)	$\epsilon \times 10^{-3}$ (mol. ⁻¹ L.cm ⁻¹)	ν (cm ⁻¹)	$\Delta\epsilon$ (mol. ⁻¹ L.cm ⁻¹)	ν (cm ⁻¹)	$\Delta\epsilon$ (mol. ⁻¹ L.cm ⁻¹)	ν (cm ⁻¹)	$\Delta\epsilon$ (mol. ⁻¹ L.cm ⁻¹)	
[Fe(R-pn(BAA) ₂)]	30,303	4.63	30,303	-8.21	32,258	+18.0			
	25,974	8.33	28,316	-432.75	29,412	-270.0	28,986	+55.27	MLCT (azomethine)
	17,094	0.03			27,027	-454.5	25,641	-458.1	MLCT (azomethine)
	16,129	0.29	23,256	+15.0	23,529	+121.3			
			17,544	-0.76	18,182	+0.8	17,094	-0.86	¹ A ₁ → ¹ A ₂
[Co(R-pn(BAA) ₂)]			28,571	+5.0	28,169	+5.0	28,571	+20.0	MLCT
	25,707	6.43	24,631	-71.0	24,510	-87.0	24,510	-114.0	MLCT
			18,692	+0.15	18,519	+0.16	18,182	+0.12	⁴ A ₁ → ⁴ B ₁
[Ni(R-pn(BAA) ₂)]·H ₂ O	28,604	11.47	26,316	+8.0	26,316	+8.0	25,974	+12.5	MLCT
	24,390	6.67			23,585	(sh)	23,530	(sh)	
	22,727	4.17	17,699	-7.4	17,544	-10.0	17,544	-11.00	¹ A ₁ → ¹ B ₂ (d _{xy}) (d _{x²-y²)}

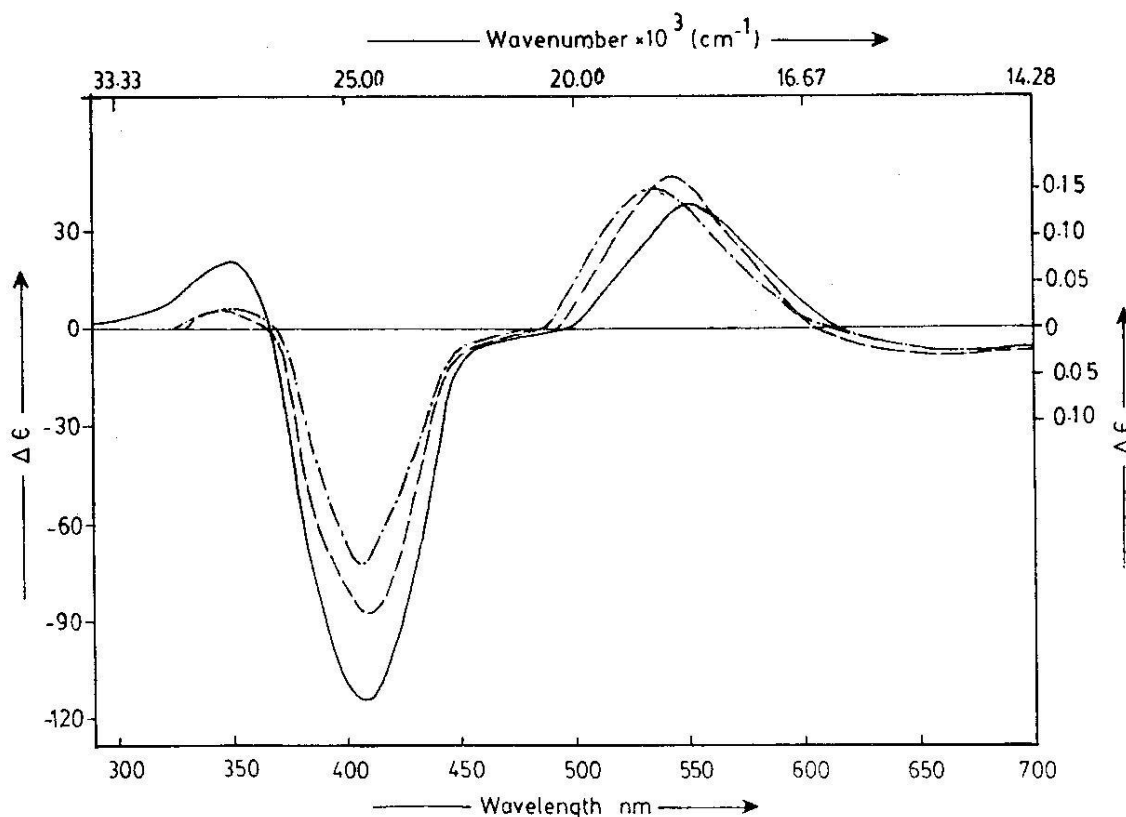


Fig. 1: CD spectrum of $[\text{Co}(\text{R-pn}(\text{BAA})_2)]$ in acetonitrile (-.-.-), chloroform (- - -) and dioxane (—) solutions.

$\text{Amp})_2 (\text{H}_2\text{O})_2]^{n+}$ $19,231 \text{ cm}^{-1}$, $[\text{Co}(++)\text{-Ceph})_2 (\text{H}_2\text{O})_2]^{n+}$ $17,857 \text{ cm}^{-1}$ and $[\text{Cr}(\text{RR-chxn}(\text{BAA})_2)]$ $16,488 \text{ cm}^{-1}$ [3].

The CD of $[\text{Ni}(\text{R-pn}(\text{BAA})_2)] \cdot \text{H}_2\text{O}$ in different solvents (Fig. 2) consists of a positive Cotton band between $25,974\text{-}26,318 \text{ cm}^{-1}$ ($\Delta\epsilon$ $8.0\text{-}12.5 \text{ M}^{-1}\text{cm}^{-1}$) and a second shoulder band is visible between $23,530\text{-}23,585 \text{ cm}^{-1}$. This shoulder band is not observed in CH_3CN solution of the complex. This CD band shifts to lower frequency in dioxane but remain unaffected in CHCl_3 or CH_3CN solutions. In the crystal field region, a strong negative band between $17,544\text{-}17,699 \text{ cm}^{-1}$ ($\Delta\epsilon$ $7.4\text{-}11.0 \text{ M}^{-1}\text{cm}^{-1}$) is observed for this complex in different solvents. This band is shifted to higher frequency in CH_3CN but remain unaltered in CHCl_3 or $\text{C}_4\text{H}_8\text{O}_2$. This band is associated with relatively higher $\Delta\epsilon$ and may be assigned to a spin allowed electronic transition ${}^1\text{A}_1 \rightarrow {}^1\text{B}_2$ ($d_{x^2-y^2} \rightarrow d_{xy}$) in a low symmetry square

planar complex. Several workers have assigned CD and absorption bands between $16,370\text{-}19,330 \text{ cm}^{-1}$ to a similar transition[4].

The CD of these two complexes are very different from analogous $\text{O}_2\text{-O}_2$ bonded $[\text{M}(\text{R-pn}(\text{BAA})_2)]$ (where $\text{M} = \text{VO}(\text{IV}), \text{Cu}(\text{II})$ and $\text{UO}_2(\text{VI})$) species reported earlier. the CD of $\text{O}_2\text{-O}_2$ bonded complexes consist of the familiar oppositely signed couplet of bands of nearly comparable molar differential absorptivity values due to azomethine. On the other hand, CD of $\text{N}_2\text{-O}_2$ bonded $[\text{Co}(\text{R-pn}(\text{BAA})_2)]$ consists of a similar couplet of band whose positive component is associated with very small value of $\Delta\epsilon$. Further, the positive component in this case lies on the higher frequency side while in $\text{O}_2\text{-O}_2$ bonded species, it is observed on the lower frequency side of the spectrum, i.e. the signs of the couplet bands are reversed in the $\text{N}_2\text{-O}_2$ bonded complexes. The CD of $[\text{Ni}(\text{R-pn}(\text{BAA})_2)] \cdot \text{H}_2\text{O}$

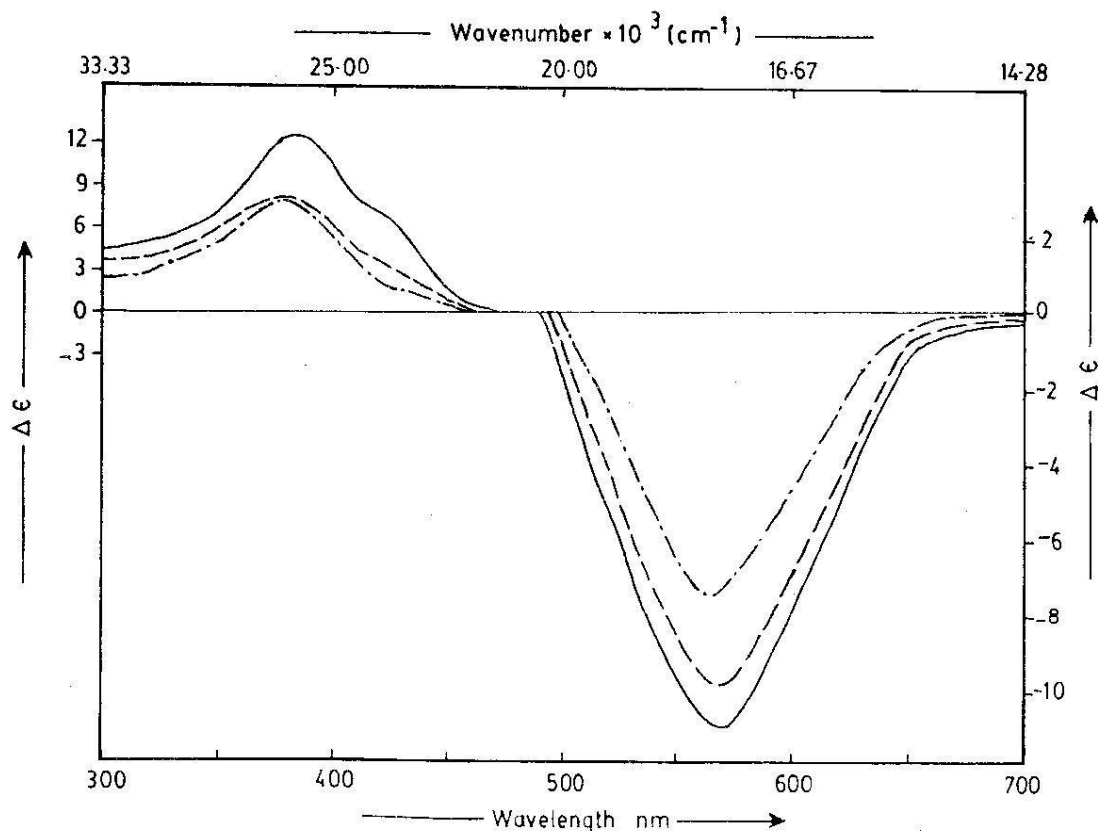
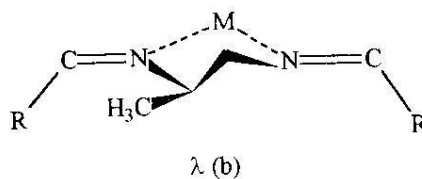
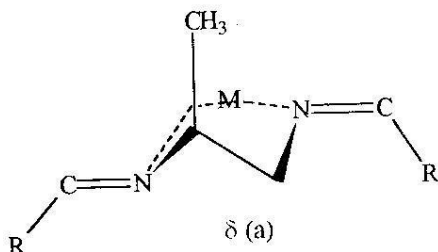


Fig. 2: CD spectrum of $[\text{Ni}(\text{R-pn}(\text{BAA})_2)\cdot\text{H}_2\text{O}]$ in acetonitrile (-.-.-), chloroform (- - -) and dioxane (—) solutions.

consists of only two positive bands and negative components is completely vanished. These differences in CD of two types of complexes may be explained considering their bonding sites.

When metal atom is bonded to $\text{N}_2\text{-O}_2$ compartment of the ligand, the conformation of azomethine chelate contributes significantly to its CD spectrum. In these complexes a conformational inversion around the asymmetric atom is possible when methyl group in pn is in δ (a) conformation and pseudoequatorial when the ring conformation is λ (b).



The relationship between these two possibilities is diastereomeric and one should predominate in solution [5]. Inspection of models shows a significant 'in plane 1,3 interaction' between the CH_3 -group (pn) and the substituents at the azomethine carbon atoms. It may be predicted that conformation (a) in which this steric hindrance is partially removed will dominate in solution.

When the metal atom is bound to the ligand through $\text{O}_2\text{-O}_2$ atoms in outer compartment, the CH_3 - in pn is free to change its conformation without affecting conformation of the expanded chelate and

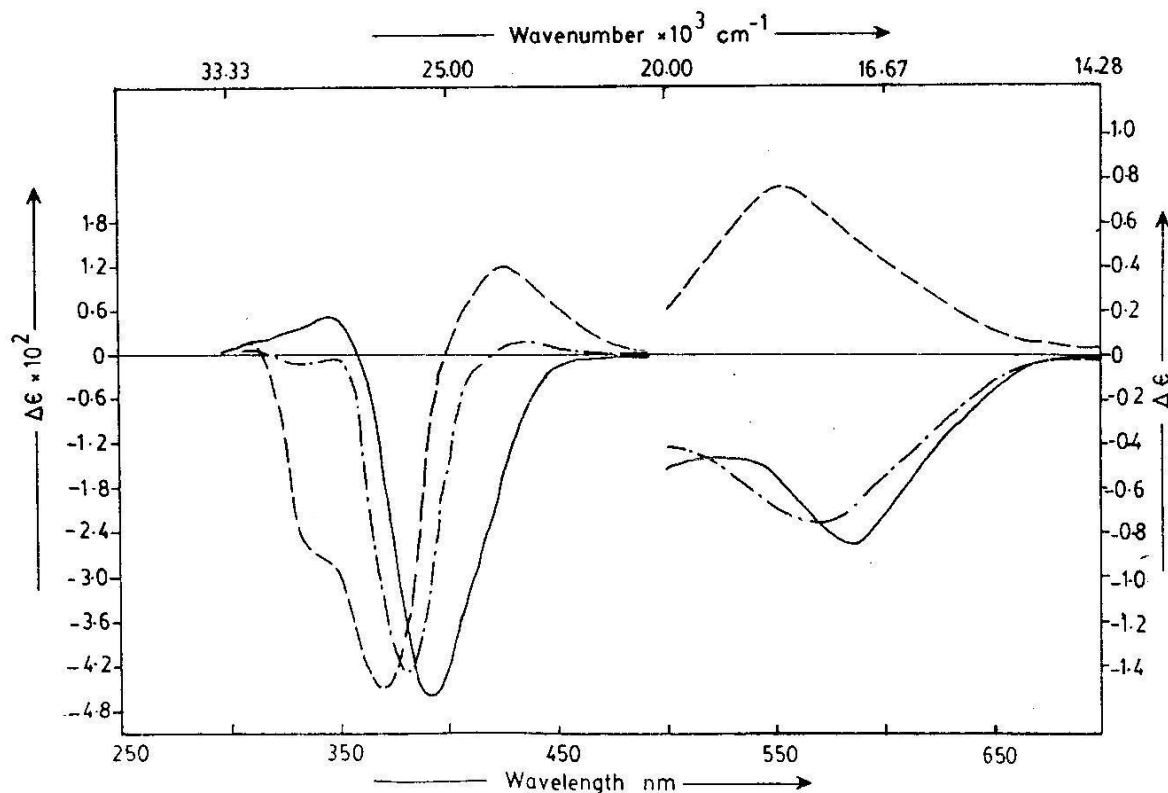


Fig. 3: CD spectrum of $[\text{Fe}(\text{R-pn}(\text{BAA})_2)]$ in acetonitrile (- · - · -), chloroform (- - -) and dioxane (—) solutions.

therefore has very little effect upon CD of the complex. This is in agreement with the observation that couplet of bands due to azomethine in $\text{O}_2\text{-O}_2$ bonded complexes remain unaffected in different solvents.

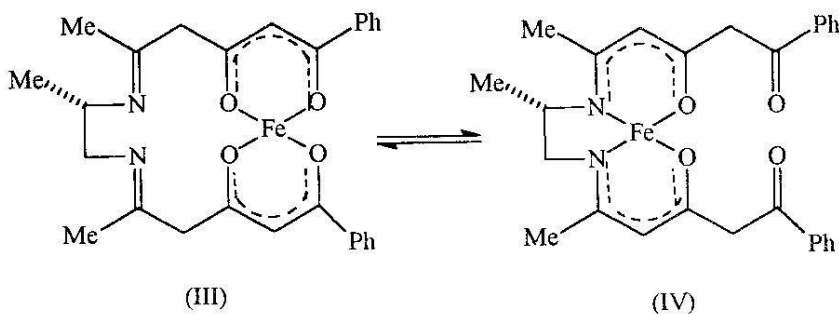
The CD spectrum of $[\text{Fe}(\text{R-pn}(\text{BAA})_2)]$ (Fig. 3) in different solvents consists of a number of oppositely signed bands in UV region but only one band between $17,094\text{-}18,182\text{ cm}^{-1}$ in the crystal field region. Further, CD bands of this complex are markedly influenced by the solvent. The CD of this complex in CHCl_3 consists of a positive Cotton band at $32,258\text{ cm}^{-1}$ ($\Delta\epsilon\ 18.0\ \text{M}^{-1}\text{cm}^{-1}$), a couple of negative bands at $29,412\text{ cm}^{-1}$ ($\Delta\epsilon\ 270.0\ \text{M}^{-1}\text{cm}^{-1}$), $27,027\text{ cm}^{-1}$ ($\Delta\epsilon\ 454\ \text{M}^{-1}\text{cm}^{-1}$) and a fourth positive band at $23,526\text{ cm}^{-1}$ ($\Delta\epsilon\ 12.1\ \text{M}^{-1}\text{cm}^{-1}$). In acetonitrile solution of this complex, two negative bands at $30,303\text{ cm}^{-1}$ ($\Delta\epsilon\ 8.0\ \text{M}^{-1}\text{cm}^{-1}$), $28,316\text{ cm}^{-1}$ ($\Delta\epsilon\ 432\ \text{M}^{-1}\text{cm}^{-1}$) and a third positive band at

$23,256\text{ cm}^{-1}$ ($\Delta\epsilon\ 15.0\ \text{M}^{-1}\text{cm}^{-1}$) are observed while in dioxane solution, a couplet of oppositely signed Cotton bands i.e. a positive band at $28,986\text{ cm}^{-1}$ ($\Delta\epsilon\ 55.27\ \text{M}^{-1}\text{cm}^{-1}$) and a negative band at $25,641\text{ cm}^{-1}$ ($\Delta\epsilon\ 458\ \text{M}^{-1}\text{cm}^{-1}$) are observed. The oppositely signed couplet bands due to azomethine chromophore in this complex may be easily identified between $23,256\text{-}25,641\text{ cm}^{-1}$ and $27,027\text{-}28,316\text{ cm}^{-1}$ in different solvents. These are similar in shape and molar differential absorptivity values to those observed for $[\text{Co}(\text{R-pn}(\text{BAA})_2)]$. The other negative CD bands at $29,412\text{ cm}^{-1}$ (in CHCl_3) and $30,303\text{ cm}^{-1}$ (in CH_3CN) probably originate from carbonyl chromophore. There is a profound effect of solvent on this band. Since the metal ion is bound through carbonyl oxygen atoms, any change in the environment around metal ion through coordination of the solvent in trans position should markedly influence the CD bands. As dioxane is probably the best coordinating solvent of the three investigated,

CD spectra of this complex in this solvent is affected to maximum extent.

In the crystal field region, CD of $[\text{Fe}(\text{R-pn}(\text{BAA})_2)]$ consists of a negative band between $17,094\text{--}17,544\text{ cm}^{-1}$ ($\Delta\epsilon\ 0.86\ \text{M}^{-1}\text{cm}^{-1}$) in dioxane and acetonitrile solutions while a positive Cotton band at $18,182\text{ cm}^{-1}$ ($\Delta\epsilon\ 0.8\ \text{M}^{-1}\text{cm}^{-1}$) is observed in CHCl_3 solution. This band may arise from electronic transition ${}^1A_1 \rightarrow {}^1A_2$ originating from a low spin, low symmetry octahedral species. This band assignment agrees well with absorption bands already reported for a number of low spin, tetragonally distorted Fe(II)-macrocyclic complexes [6].

The influence of solvent upon CD of this complex is indicated by a successive shift in band towards lower frequency. The reversal of sign of Cotton band in CHCl_3 solution is significant. These changes in position and sign of some Cotton bands in different solvents indicate that in solution, Fe(II) shifts from $\text{O}_2\text{-O}_2$ to $\text{N}_2\text{-O}_2$ compartment and an equilibrium between the two species is maintained.



In CHCl_3 solution, there is an appreciable proportion of III giving CD which resembles with that of analogous VO(II) and Cu(II) complexes. On the other hand in dioxane solution, CD of this complex resembles with that of Co(II) complex suggesting that IV is predominant. The reversal of sign of CD in C.F. region in CH_3CN and dioxane solutions may be due to formation of octahedral species upon coordination of solvent molecules in axial position.

It was proposed by Bosnich [7] that observation of an oppositely signed CD couplet due

to azomethine indicated non-planarity of the two azomethine chromophores resulting a flattened tetrahedral arrangement of donor atoms around the metal. It was also predicted that if the configuration was Λ , the negative component of the azomethine couplet will lie at higher energy.

The azomethine couplet bands in $[\text{Co}(\text{R-pn}(\text{BAA})_2)]$ and $[\text{Fe}(\text{R-pn}(\text{BAA})_2)]$ (in dioxane) have their negative components on lower energy side and therefore should have Δ absolute configuration around the metal ions. The CD of $[\text{Ni}(\text{R-pn}(\text{BAA})_2)]\cdot\text{H}_2\text{O}$ consists of only positive bands in UV region indicating that Ni(II) has a square planar arrangement of $\text{N}_2\text{-O}_2$ donor atoms. The positive Cotton band at $26,315\text{ cm}^{-1}$ corresponds to positive component of azomethine couplet and may be assigned a Δ absolute configuration around Ni(II) ion as well.

It is concluded from the proceeding discussion that CD spectra of complexes of chiral Schiff bases may be used to determine chirality around the metal ions containing chiral centres in

the chelate. The CD of these complexes is influenced by the solvent. The observed Cotton bands may be assigned to electronic transitions to unidimensional energy states arising from low symmetry of these complexes.

Experimental

Materials

Analytical reagent grade solvents obtained from commercial sources were used after drying and distillation for recording spectra of these complexes. The synthesis and characterization of complexes,

[Co(R-pn(BAA)₂)], [Ni(R-pn(BAA)₂)]·H₂O and [Fe(R-pn(BAA)₂)] has already been reported elsewhere [1].

Instrumentation

The circular dichroism spectra were measured on Jasco-20A spectropolarimeter using 10 mm cylindrical quartz cells. Absorption spectra in CHCl₃ solutions were measured on Shimadzu UV-265 spectrophotometer using a matched pair of quartz cuvettes. All spectra were obtained at room temperature (~ 25°C). Solutions of concentration ranging 10⁻³-10⁻⁵ mol/dm³ were used to record these spectra.

Acknowledgement

The authors gratefully acknowledge the financial support provided by University Grants Commission, Islamabad.

References

1. N. Ahmad, R. Ahmad, S. Iqbal, *Indian J. Chem. Sec. A.*, submitted.
2. N. Ahmad, R. Ahmad, S. Iqbal, *Turkish, J. Chem.*, submitted.
3. a) N. Ahmad, C. Munir, M. Jamil and S. Rauf, *J. Chem. Soc. Pak.*, **15**, 190 (1993).
b) N. Ahmad, C. Munir and M. Jamil, *J. Chem. Pak.*, **17**, 149 (1995).
c) N. Ahmad, J. Safder and C. Munir, *Indian J. Chem. Sec A*, **20**, 214 (1995).
d) R. Ahmad, N. Ahmad, M.A. Malik, G. Snatzke and U. Wagner, *J. Chem Soc. Pak.*, **14**, 275 (1992).
4. a) R.S. Dowing and F.L. Urbach, *J. Am. Chem. Soc.*, **92**, 5861 (1970).
b) A. Merle, D. Dartiguenave and Y. Dartiguenave, *J. Mol. Struct.*, **13**, 413 (1972).
c) Y. Nishida, K. Hayashida, N. Oishi and S. Kida, *Inorg. Chim. Acta.*, **38**, 213 (1980).
5. R.S. Downing, F.L. Urbach, *J. Am. Chem.Soc.*, **91**, 5977 (1969).
6. (a) D.D. Watkins Jr., D.P. Riley, J.A. Stone and D.H. Busch, *Inorg. Chem.*, **15**, 387 (1976).
(b) D.P. Riley, J.A. Stone and D.H. Busch, *J. Am. Chem. Soc.*, **99**, 767 (1977).
7. B. Bosnich, *J. Am. Chem.*, **90**, 627 (1968).