

Circular Dichroism Studies of Metal Complexes with a Chiral Schiff Base: RR-Trans-N,N-Cyclohexane-Bis (1-Phenyl-5-imino-1, 3-hexadione)

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Summary: A series of four metal complexes ($M = VO^{2+}, Co^{2+}, Cu^{2+}, UO_2^{2+}$) of a Schiff base RR-trans-N,N-1,2-cyclohexane-bis (1-phenyl-5-imino-1,3-hexadione[RR-chxn (HBAA)₂]) have been characterized. Their infrared studies indicate that these metals are coordinated to four carbonyl oxygen atoms of the ligand while nitrogen atoms at azomethine remain uncoordinated. The circular dichroism and electronic absorption spectra of these complexes are measured in different solvents. The CD spectra of these chelates reveal more band multiplicity than do the corresponding absorption spectra. The CD spectra are correlated to various electronic transitions originating from the ligand and d orbitals of the metal ion.

Introduction

Circular dichroism studies of metal complexes are very useful as their interpretation yield valuable information concerning the origin of electronic transitions in such systems. These spectra may be easily interpreted because of narrower band widths and sometimes oppositely signed bands. In addition, CD is very sensitive to molecular framework and considerable information about conformation and configuration of chelates may be obtained.

A series of tetradentate Schiff bases have been synthesized by condensing two molecules of diketones or some aldehydes (like salicylaldehyde) with one mole of 1,2-diamines. If chiral diamines (such as 1,2-diaminopropane, 2,3-diaminobutane or trans 1,2-diaminocyclohexane) are condensed with a diketone, the resulting Schiff bases behave as chiral quadridentate ligands. In the past, a number of workers have utilized CD spectra of copper (II), nickel (II), zinc(II) and oxovanadium(IV) chelates of such ligands for determining the preferred chelate conformation and donor atom configuration [1-4]. It has also been reported that a chiral Schiff base R,R-trans-N,N-1,2-cyclohexane-bis (4-imino-2-pentanone) failed to form chelates in aqueous solution [5]. Later studies revealed that chelation of copper(II) with this ligand does not occur even under rigorously anhydrous conditions [1]. This was attributed to severe interaction between the methyl

substituents at the azomethine carbon and the bridging cyclohexane group.

Condensation of triketones with 1,2 diamines yield "compartmental ligands" capable of forming mono and binuclear chelates [6]. However, CD studies of chelates of chiral Schiff bases of triketones have never been investigated to our knowledge. Mono and binuclear chelates of such ligands are of special interest because they are only soluble in organic non-coordinating solvents and so retain their molecular structure in solutions as well.

We wish to report CD studies of a number of mononuclear metal chelate complexes with a chiral Schiff base i.e. R,R-trans-N,N-1,2-cyclohexane-bis (1-phenyl-5-imino-1,3-hexadione) (R,R-1,2-chxn (HBAA)₂). We are particularly interested in comparing the chelation behaviour of this ligand with that of the analogous derivatives of 2,4-pentanedione and determining the conformation of the cyclohexyl group in these chelates.

Results and Discussion

The compounds [VO(R,R-chxn(BAA)₂], [Co(R,R-chxn(BAA)₂)], [Cu(R,R-chxn(BAA)₂)], and [UO₂(R,R-chxn(BAA)₂)] are easily obtained by reaction of respective metal salts with the chiral ligand from mixed solvent CHCl₃-C₂H₅OH as

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Table 1: Color, decomposition points and prominent infrared bands of metal complexes of chiral Schiff base RR-chxn(HBAA)₂

Complex	Color	Decom. point	Infrared bands (cm ⁻¹)							
			ν_{θ}	$\nu_{\theta_{C=N}}$	ν	ν_{C-H}	ν_{C-H}	ν_{C-N-C}	$\nu_{M=O}$	ring bending
[VO(R,R-chxn(BAA) ₂)]	Bluish green	309	2938	1605 (m)	1491	1467	1383	1146	909	875
[Co(R,R-chxn(BAA) ₂)]	Dark red	289	2944	1611	1524	1467	1335	1350	1146	882
[Cu(R,R-chxn(BAA) ₂)]	Yellowish green	225	2938	1614	1527	1473	1335	1146		882
[UO ₂ (R,R-chxn(BAA) ₂)]	Dark maroon	226	2938	1605	1491	1464	1386	1146	909	693

m = multiplet

orange to green solids. These compounds decompose between 224-308^o C and easily dissolve in many donor solvents as well as in chloroform except Cu(R,R-chxn(BAA)₂) which dissolve only in pyridine. Their elemental analyses show that one ligand is attached to one metal atom. For the purpose of analyses, these compounds were thoroughly dried in a drying pistol under high vacuum, therefore it is possible that coordinated solvent if present, is also evacuated. The melting points and prominent infrared bands of these complexes are give in Table 1.

The infrared spectra of these compounds in KBr phase show that the characteristic carbonyl stretching band present at 1590 cm⁻¹ in the ligand undergoes a change in its intensity, shape and position. This band is shifted to lower frequency. In fact, a well defined band due to free carbonyl stretching is not observed in any of these complexes. This clearly indicates that all carbonyl oxygens are coordinated to metal ions. The bands due to C-N-C and -C=N stretching vibrations remain unchanged in these complexes. These observations strongly support that the ligand is bound to the metal ion through four oxygen donors from carbonyls while nitrogen atoms remain uncoordinated. This is in accordance with the earlier observations that analogous R,R-chxn(acac)₂ does not coordinate with metal ions due to severe interaction between methyl at the azomethine and the bridging cyclohexylene group. Inspection of models show that there is severe interaction between these two groups of the ligand and that the nitrogen atoms move farther away (making a bigger cavity, unsuitable for coordination) to overcome this steric hinderance. The VO- and UO₂- chelates have char-

acteristic strong vibrational band due to M=O at 909 cm⁻¹. In the lower frequency region stretching vibrations due to M-N are not visible.

The circular dichroism spectra of these chelates are presented in Figures 1-2. The absorption and CD band positions along with extinction coefficients and differential absorptivity ($\Delta\epsilon$) values are given in Table 2. The absorption spectra of these complexes were recorded in chloroform solution except that of copper(II) which was taken in pyridine. The CD spectrum of each complex was measured in its respective solvent. The absorption spectrum of the ligand consists of four high intensity bands centered at 25,660 (III), 30,921(II), 40,750(1a) and 48,170 (Ib) cm⁻¹. Their extinction coefficients are of the order 2.6-29.6 x 10⁴ M⁻¹cm⁻¹. The higher energy bands 1a and 1b seem to originate from $\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the benzene ring while bands II and III arise from azomethine chromophore due to enolate form and belong to $\pi \rightarrow \pi^*$ transitions. The absorption spectra of these complexes consist of 2-3 high intensity bands between 40,339 - 23,883 cm⁻¹ in UV region. The higher energy transitions due to benzene ring in the ligand are observed as a single band in the VO(II) and Co(II) complexes at 40,339 and 38,912 cm⁻¹ respectively. The band due to the azomethine chromophore in the ligand is slightly shifted to lower energy in these complexes. This band has undergone a bathochromic shift of nearly 616-1252 cm⁻¹ as was observed for Schiffs bases of 1,2-diketone chelates. These observations also support the coordinate bonding mentioned earlier i.e. the four oxygen donors from the carbonyl part of the ligand are coordinated. The absorption spectrum of the Cu(II) chelate complex in pyridine

Table 2: Absorption and circular dichroism spectra of the ligand and complexes of chiral Schiff base.

Complexes	Solvent	Absorption		Solvent	Circular dichroism	
		ν_{\max} cm^{-1}	$E \times 10^{-4}$ $\text{M}^{-1} \text{cm}^{-1}$		ν_{\max} cm^{-1}	$\Delta\epsilon$ $\text{M}^{-1} \text{cm}^{-1}$
[RR-chxn(HBAA) ₂]	CHCl ₃	25,660 (III)	4.28	EtOH	25,157	- 116.3
		30,921 (II)	2.60		27,933	+ 36.49
		40,766 (Ia)	2.77		32,258	+ 27.70
		48,170 (Ib)	29.59		37,665	+ 6.96
[VO(RR-chxn(BBA)) ₂]	CHCl ₃	25,044 (III)	2.33	CHCl ₃	44,693	+ 2.56
		30,377 (II)	1.63		23,980	- 86.11
		40,339 (I)	3.12		27,435	+ 19.37
		30,221 (II)	1.65		32,258	+ 23.08
[Co(RR-chxn(BAA)) ₂]	CHCl ₃	24,408 (III)	2.38	CHCl ₃	15,117	+ 0.21
		30,221 (II)	1.65		16,639	- 0.45
		38,911 (I)	2.56		23,148	- 113.45
					25,974	+ 59.96
[Cu(RR-chxn(BAA)) ₂]	C ₅ H ₅ N	23,883	5.27	C ₅ H ₅ N	31,397	+ 13.45
		25,947	4.8		37,736	+ 13.45
					14,588	+ 0.03
					16,488	- 0.23
[UO ₂ (RR-chxn(BAA)) ₂]	CHCl ₃	25,934 (III)	2.61	Dioxane	23,283	- 19.64
		30,664 (II)	1.47		25,907	+ 9.46
					31,696	+ 2.64
					37,523	+ 1.54
				42,283	+ 1.67	
				14,837	- 0.245	
				17,606	+ 0.089	
				23,952	- 41.34	
				27,739	+ 42.36	
				44,346	+ 4.70	

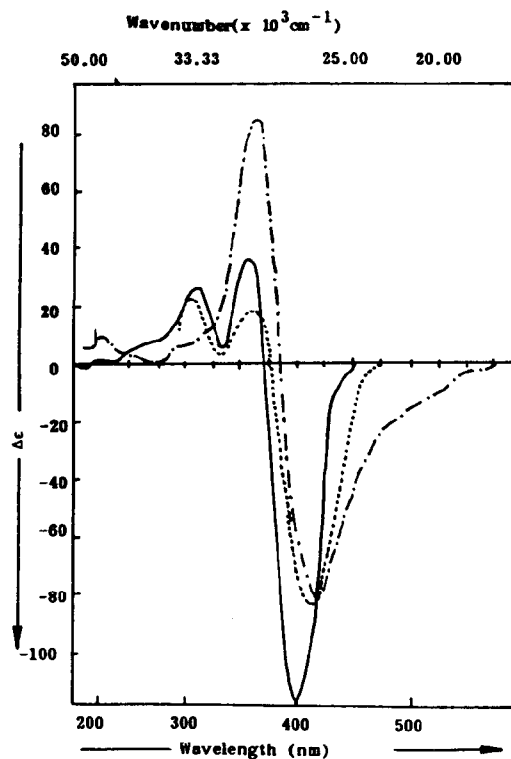


Fig. 1: Circular dichroism spectra of (a) R,R-chxn(HBAA)₂ in chloroform (-----) (b) VO(RR-chxn(BAA))₂ in chloroform (.....) (c) UO₂(RR-chxn(BAA))₂ in dioxane (-.....).

consists of two bands at 23,883 and 25,947 cm^{-1} . For this complex, pyridine is perhaps coordinated in trans positions which has strong absorption in UV region. Therefore, bands due to the phenyl ring have been masked and only the two bands originating from charge transfer transitions from the carbonyl chromophore are seen.

The CD spectrum of the ligand in ethanol solution consists of a negative Cotton band at 25,157 cm^{-1} and four positive Cotton bands at 27,993, 32,258, 37,665 and 44,643 cm^{-1} . The differential absorptivity ($\Delta\epsilon$) of the negative band is of the order of 116.3 $\text{M}^{-1} \text{cm}^{-1}$ while that of remaining bands is between 2.56-36.49 $\text{M}^{-1} \text{cm}^{-1}$. The negative Cotton band at 25,157 cm^{-1} and positive band at 27,933 cm^{-1} constitute the couplet bands observed for a number of other chiral tetradentate Schiff bases derived from condensation of R,R-trans 1,2-diamino-cyclohexane and aldehydes. This couplet has been interpreted as excitation component of the $\pi \rightarrow \pi^*$ band of the azomethine chromophore [10].

The CD spectra of VO²⁺, Co²⁺ and UO₂²⁺ complexes consist of three to four Cotton bands between 23,148-44,346 cm^{-1} . The first lower frequency band is invariably very intense and negative in sign

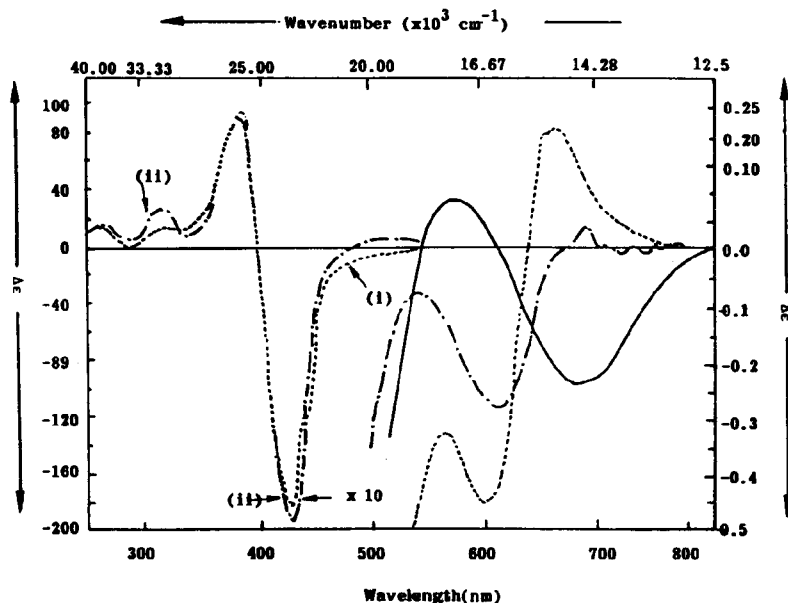
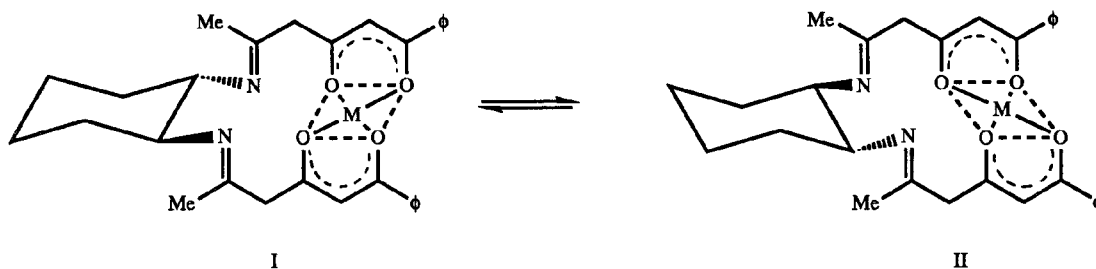


Fig. 2: Circular dichroism spectra of (a) Co(RR-chxn(BAA)₂ in chloroform (-----) and (ii) Dioxane (-.-.-.-) and (b) Cu(R,R-chxn(BAA)₂ in pyridine (_____).

while remaining bands have low differential absorptivity and are of positive sign. The couplet bands due to azomethine may be identified at 23,981 cm^{-1} and 27,435 cm^{-1} for VO^{2+} , 23,148 cm^{-1} and 25,974 cm^{-1} for Co^{2+} and 23,952 cm^{-1} and 27,739 cm^{-1} for UO_2^{2+} chelates. These couplet bands due to azomethine are somewhat displaced but their sign and shape remains unaltered upon complexation. Since azomethine nitrogen atoms are not coordinated in these systems, they are free to assume the preferred and most stable conformation depicted in I. Therefore, CD bands (due to azomethine) in these complexes do not change sign upon chelation as was observed for Cu(R,R-chxn(sal)₂ and VO(SS-chxn(sal)₂ complexes [1]. A positive weak Cotton band observed at 44,643 cm^{-1} for the ligand is also found in UO_2^{2+} (at 44,346 cm^{-1}) and Co^{2+} (at 42,283 cm^{-1}) complexes.

This band is due to the benzenoid chromophore and least affected upon coordination. Similarly two positive bands observed at 32,258 cm^{-1} and 37,665 cm^{-1} in the ligand are present as one band in VO^{2+} (at 32,258 cm^{-1}) or Co^{2+} (at 37,523 cm^{-1}) chelates.

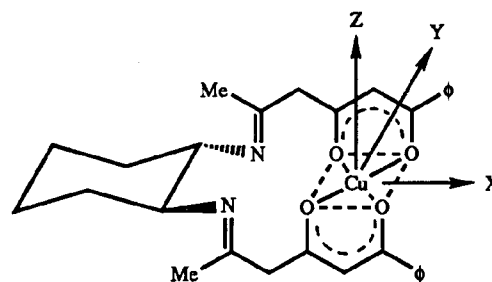
The CD spectrum of Co(R,R-chxn(BAA)₂ was measured in chloroform as well as in dioxane. Although band positions do not differ to a larger extent in the two solvents, their molar ellipticities are very much decreased in dioxane solution as compared to those in chloroform. In addition an extra positive Cotton band is observed at 42,283 cm^{-1} for this complex in dioxane. The high frequency Cotton bands at 42,283 cm^{-1} and 37,523 cm^{-1} in this complex are due to benzenoid chromophore while couplet bands with oppositely signed components corresponding to azomethine are observed at



23,148 cm^{-1} and 25,974 cm^{-1} . The positive Cotton band at 31,397 cm^{-1} belongs to a charge transfer transition $\text{Co} \rightarrow \text{L}$.

In the d-d transition region, the CD spectrum of $\text{Co}(\text{R,R-chxn}(\text{BAA})_2)$ consists of a Cotton band couplet, a positive band at 15,177 cm^{-1} ($\Delta\epsilon$ 0.21) and a negative band at 16,639 cm^{-1} ($\Delta\epsilon$ 0.45). The CD of $\text{Cu}(\text{R,R-chxn}(\text{BAA})_2)$ in pyridine solution also consists of two Cotton bands of opposite sign, a negative band at 14,837 cm^{-1} ($\Delta\epsilon$ 0.245) and a second positive band at 17,600 cm^{-1} ($\Delta\epsilon$ 0.089). The chiral center in these complexes is present in the farthest part of ligand many atoms away from the chelate ring. The conformation around the chiral center may be easily interchanged without causing much strain in the chelate ring. Therefore, CD bands due to d-d transitions are not expected to be largely affected by the chiral centers. The signs of these bands in $\text{Co}(\text{II})$ and $\text{Cu}(\text{II})$ chelates are reversed due to difference in the origin of electronic transitions. Also there is a difference of environment around the two complexes i.e. cobalt(II) attains a six coordinated octahedral geometry while copper(II) prefers a square planar four coordination or a distorted octahedral six coordination. Assuming an octahedral environment around cobalt(II) chelate, these CD bands may be assigned to transition from split ${}^4\text{T}_{1g}$ level to non-degenerate ${}^1\text{A}_{2g}$ upper state. The two bands in this complex are quite close ($\Delta\nu$ 1522 cm^{-1}) and arise from the split ground state level ${}^4\text{T}_{1g}$. The absorption spectra of a number of six coordinated cobalt(II) complexes have been measured and bands between 13,300-18,400 cm^{-1} have been assigned as transition to the ${}^4\text{A}_{2g}$ upper state [11]. As symmetry of this complex is low (C_2) the ground and first excited state energy levels (i.e. ${}^4\text{T}_{1g}$ and ${}^4\text{T}_{2g}$) are split into non-degenerate A, B levels. In this symmetry two transition $\text{B}_1 \rightarrow \text{A}_1$ and $\text{A}_2 \rightarrow \text{A}_1$ are CD allowed by electric as well as magnetic dipole moments while the third transition $\text{A}_1 \rightarrow \text{A}_1$ is forbidden for these considerations. Therefore, positive Cotton band at 15,117 cm^{-1} may be assigned to ${}^4\text{B}_1 \rightarrow \text{A}_1$ while the higher frequency negative band observed at 16,639 cm^{-1} is due to ${}^4\text{A}_2 \rightarrow \text{A}_1$ transition.

The ground state in square planar copper(II) chelates taking the molecular framework in the xy plane (as shown) has the d_{xy} orbital singly occupied [1a]. It has been shown for $\text{Cu}(\text{II})$ - β -diketonates that the four filled d-orbitals are closely spaced and



III

lie at about 20,000 cm^{-1} below the d_{xy} orbital [12]. Therefore, all d-d transitions may be expected to occur within the broad absorption band commonly observed for square planar copper(II) complexes [13]. The low symmetry complex $\text{Cu}(\text{R,R-chxn}(\text{BAA})_2)$ (C_2) has only non-degenerate energy levels. In this case all d-d transitions are allowed from selection rules and are expected to give rise to stronger CD bands. The negative CD band observed at 14,837 cm^{-1} in this chelate may be assigned to $d_{z^2} \rightarrow d_{xy}$ (${}^2\text{A}_1 \rightarrow {}^2\text{B}_2$) transition while the positive band at 17,606 cm^{-1} originate from $d_{x-y} d_{xy}$ (${}^2\text{A}_1 \rightarrow {}^2\text{B}_1$) transition in agreement with the predictions of simple crystal field theory [14]. These CD band assignments are consistent with those proposed by Downing *et al* [1] for a number of copper(II) chelates of tetradentate Schiff base ligands. These workers assigned positive CD bands between 13,890 - 14,490 cm^{-1} and negative bands between 17,360 - 18,180 cm^{-1} to these transitions for a number of chelates. The reversal of sign of Cotton bands in $[\text{Cu}(\text{R,R-chxn}(\text{BAA})_2)]$ is perhaps due to the fact that four oxygen donors are bound to the metal atom while, in reference compounds, two nitrogens and two oxygens were coordinated with the metal thus locking the asymmetric atoms in a particular conformation.

Experimental

a. Materials

Trans-1,2-diaminocyclohexane obtained from Aldrich, was resolved by a literature method [7], $[\alpha]_{\text{D}}^{20}$ for R,R-chxn = -40 lit. = -36 [8]. 1-Phenyl-1,3,5-hexanetrione (H_2BAA) was synthesized by Miles *et al.* method [9]. All other reagents used were of analytical reagent grade and used without further purification.

b. Synthesis of RR-trans-N,N-1,2-cyclohexane bis-(1-phenyl-5-imino-1,3-hexanedione

A hot solution of R,R-1,2-diaminocyclohexane (0.01 mole) in 5 ml of ethanol containing 0.02 mole LiOH was mixed with a hot solution of 1-phenyl-1,3,5-hexanetrione (0.02 mole) in 10 ml ethanol and the mixture was heated on a water bath for 5 minutes and allowed to cool. The precipitated product was filtered and recrystallized from ethanol. Yield = 90.5%, Anal. Calcd. for $C_{30}H_{34}N_2O_4$: C 74.07, H 7.00, N 5.76%. Found: C 74.02; H 7.03; N, 5.73%. UV λ_{max} (EtOH) nm (ϵ) = 261 (1.02×10^4), 324 (2.04×10^4), 396 (2.96×10^4). NMR ($CDCl_3$) δ ppm = 1.25 - 1.4 (4H, m, CH_2 of cyclohexane), 1.59 (3H, s, CH_3), 1.68 (3H, s, CH_3), 1.85 (2H, s, CH_2 of chxn), 1.91 (2H, s, CH_2 of chxn), 3.1 - 3.29 (2H, m, CH of chxn), 3.82 - 3.95 (18H, m, CH_2 of BAA), 4.5 - 5.15 (2H, m, CH = of BAA), 7.5 - 8.15 (10H, m, aromatic), 10.3 - 10.42 (1H, dd, NH), 10.98 - 11.00 (1H, dd, NH) 15.70 - 15.8 (1H, d, OH).

c. Synthesis of complexes

i. R,R-Trans-N,N-1,2-cyclohexane-bis(1-phenyl-5-imino-1,3-hexanedionato)oxovanadium(IV), [VO(R,R-chxn(BAA))₂].

It was prepared by separately dissolving 0.486 g (1 mole) of the ligand in 50 ml of chloroform and 0.217 g (1 mole) of vanadyl sulphate in 30 ml of methanol, warming them to 40° and then mixing in a reaction flask. A slight excess of Et_3N (0.15 g, 1.5 mole) was added to the reaction mixture and then refluxed for 2 hours. The solvent was removed by evaporation. The residue was washed with $CHCl_3$ to remove unreacted ligand and then with water to remove metal salt and finally with cold water. The complex was recrystallized from acetone/methanol (1:1) mixture. It was further dried in a drying pistol (benzene) under high vacuum. Anal. Calcd. for VO ($C_{30}H_{32}N_2O_4$): C, 65.30; H, 5.80; N, 5.08; V, 9.24%. Found: C 65.50; H 5.91; N 5.10; V 9.14%.

ii. R,R-Trans-N,N-1,2-cyclohexane-bis(1-phenyl-5-imino-1,3-hexanedionato)cobalt(II), [Co(R,R-chxn(BAA))₂].

This was prepared in a manner analogous to the preparation of the previous complex using cobalt(II) acetate. The complex was recrystallized from acetone and dried in drying pistol under high

vacuum. Anal. Calcd. for $Co(C_{30}H_{32}N_2O_4)$: C, 66.26; H, 5.89; N, 5.15; Co, 10.85 %. Found: C, 66.52; H 5.94; N, 5.35; Co 10.71%.

iii. R,R-Trans-N,N-1,2-cyclohexane-bis(1-phenyl-5-imino-1,3-hexanedionato)copper(II), [Cu(R,R-chxn(BAA))₂].

This was also prepared by mixing equimolar quantities of the ligand and $Cu(OAc)_2$ as described in (i) above. It could not be recrystallized from a suitable solvent. It was dried in a drying pistol under high vacuum. Anal. Calcd. for $Cu(C_{30}H_{32}N_2O_4)$: C, 65.72; H, 5.84; N, 5.11; Cu 11.6%. Found: C, 65.60; H 5.71, N, 4.99; Cu, 11.70%.

iv. R,R-Trans-N,N-1,2-cyclohexane-bis(1-phenyl-5-imino-1,3-hexanedionato)dioxouranium(VI), [UO₂(R,R-chxn(BAA))₂].

This was prepared from uranyl acetate and ligand in a manner analogous to the previous complex. The complex was recrystallized from acetone/ethanol (1:1) mixture and dried as described earlier. Anal. Calcd. for $UO_2(C_{30}H_{32}N_2O_4)$: C, 47.73; H, 4.24; N, 3.71%. Found: C, 47.56; H, 4.04, N 3.80%.

d. Physical measurements

The solution absorption spectra in chloroform were measured on a Philips model PU8700 spectrophotometer using 0.01 - 0.2 cm quartz cuvettes. Circular dichroism spectra were recorded on a ISA-JOBIN-Yvon Dichrograph Mark III. CD measurements were made in different solvents and in varying path lengths. The quartz cells of 0.01 - 2.0 cm thickness were used for recording the spectra. The infrared spectra of solid compounds in KBr disc were recorded on Hitachi model 270-50 spectrophotometer. NMR studies were made on Bruker model AM-400 spectrometer. Elemental analysis were made on Carlo Erba-STRUM model DP-200.

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