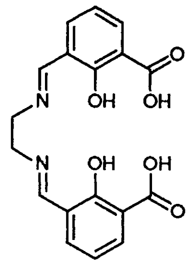
Cobalt(II)–Lanthanoid(III) (Ln = La, Nd, or Gd) Complexes of *N,N'*-Ethylenebis(3-carboxysalicylideneimine). Interaction of Ligating Groups on the Co–Ln Centre†

Yūichiro Aratake, Hisashi Ōkawa,* Eiji Asato, Hiroshi Sakiyama, Masahito Kodera, and Sigeo Kida
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashiku, Fukuoka 812, Japan
Masatomi Sakamoto
Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Bunkyo-cho, Matsuyama 790, Japan

Cobalt(II)–lanthanoid(III) complexes of *N,N'*-ethylenebis(3-carboxysalicylideneimine) (H_4csalen), [CoLa(csalen)(CH_3OH)(NO_3)], [CoNd(csalen)(H_2O)$_2$(NO_3)], and [CoGd(csalen)(H_2O)(NO_3)], have been prepared and characterized, where the cobalt ion is bound at the N_2O_2 site and the lanthanoid ion at the O_4 site of the binucleating ligand. Based on electronic and e.s.r. spectra the configuration around the cobalt ion was shown to be planar at room temperature in dimethylformamide (dmf) or dimethyl sulphoxide (dmso) while square pyramidal at liquid-nitrogen temperature with a solvent molecule at the axial site. When a nitrogen-containing base such as pyridine or n-propylamine was added to dmf solutions of the Co–Ln complexes the base was co-ordinated to the cobalt ion to afford five-co-ordination around the metal at room temperature. At liquid-nitrogen temperature the configuration around the cobalt was dependent upon the nature of the added base: six-co-ordination for pyridine or its derivatives and five-co-ordination for aliphatic amines. It is suggested that substrates possessing N- and O-donor groups such as 2-aminoethanol are specifically bound at the Co–Ln centre, *via* N to the cobalt and O to the lanthanoid ion.

The chemistry of heteronuclear metal complexes is the subject of many recent studies concerning the properties and reactivity associated with such heteronuclear systems,[1] the mimicry of the active sites of some metalloenzymes like bovine erythrocyte superoxide dismutase[2] and cytochrome c oxidase in mitochondrial respiration,[3] and the spin-exchange mechanism between paramagnetic metal ions.[4] So far much effort has been devoted to the development of binucleating ligands[5–7] that can afford discrete heterobinuclear metal complexes. As such ligands we have developed *N,N'*-ethylenebis(3-carboxysalicylideneimine) (H_4csalen) and its homologues which possess two dissimilar co-ordination sites, N_2O_2 and O_4, sharing the bridging phenolic oxygens.[8] These ligands form a series of discrete heterobinuclear complexes[8–15] by incorporating a transition-metal ion higher in the Irving–Williams order into the N_2O_2 site and a transition-metal ion lower in the order into the O_4 site. Further, they form heterobinuclear complexes with a transition-metal ion at the N_2O_2 site and a lanthanoid or non-transition-metal ion at the O_4 site,[16,17] which will be referred to as *d–f* and *d–p* binuclear complexes, respectively.

Recently we have reported[16] that the Cu^{II}–Ln^{III} [Ln^{III} = lanthanoid(III) ion] complexes of H_4csalen show unique 'selective solvations' associated with copper or lanthanoid centre, depending upon the nature of the solvent. That is, in nitrogen-containing solvents like pyridine the solvation occurs preferentially at the copper centre, whereas in oxygen-containing solvents like dimethylformamide (dmf) or dimethyl sulphoxide (dmso) it occurs at the lanthanoid centre while maintaining the planar configuration around the copper ion. This selective solvation has been extended to specific binding of substrates, that possess a N and an O donor atom, on the Cu^{II}–Gd^{III} centre.[18] In this study we report the synthesis and characterization of Co^{II}–Ln^{III} (Ln = La, Nd, or Gd) complexes of H_4csalen and interactions of various ligating groups at the Co–Ln centre.



Experimental

Materials.—3-Formylsalicylic acid was obtained by the modified Duff reaction.[19] The ligand was prepared by the literature method.[20] All chemicals were of reagent grade and were used as commercially purchased. Solvents used for preparations and measurements were purified in the usual ways and degassed before use.

Preparations of Complexes.—Preparations of metal complexes were carried out under argon or nitrogen by the use of a Schlenk apparatus or VAC model HE-43-2 inert atmosphere and vacuum deposition equipment. The complex [Co(H_2csalen)(py)$_2$] (py = pyridine) was prepared according to the method

---

† *Non-S.I. unit employed:* G = 10^{-4} T.

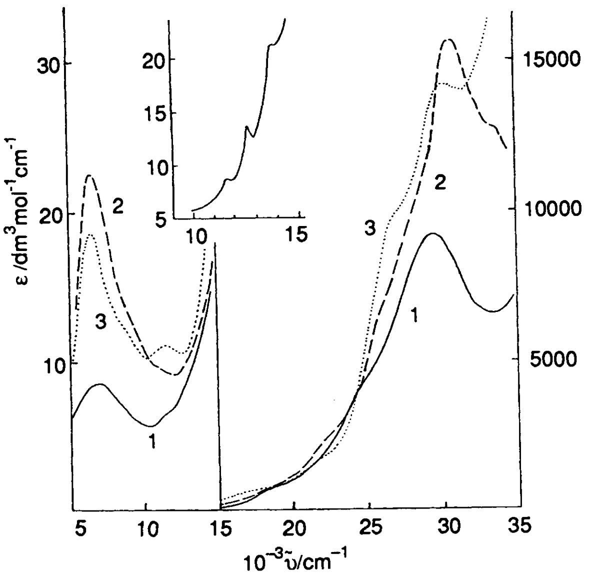


Figure 1. Electronic spectra of the Co–La complex in dmf (trace 1), in dmf with pyridine (2), and in dmf with n-propylamine as the added base (3). Concentration 1×10^{-3} mol dm^{-3}, [Co–La]/[base] = 1:10, at room temperature. The insert is the near-i.r. spectrum of the Co–Nd complex in dmf

of Torihara *et al.*[12] and [Co(H_2csalen)] by the method of Zarembowitch *et al.*[21]

Li_2[Co(csalen)(py)]·2.5H_2O. The ligand H_4csalen (500 mg), cobalt(II) acetate tetrahydrate (500 mg), and LiOH·H_2O (920 mg) were dissolved in methanol (10 cm^3)–pyridine (15 cm^3). The solution was refluxed for 3 h, filtered, and concentrated to a small volume to give reddish orange microcrystals. These were separated by filter suction and dried *in vacuo*. Yield 69% (Found: C, 50.60; H, 3.90; Co, 10.45; N, 7.60. Calc. for $C_{23}H_{22}CoLi_2N_3O_{8.5}$: C, 50.30; H, 4.05; Co, 10.70; N, 7.65%).

[CoLa(csalen)(CH_3OH)(NO_3)]. To [Co(H_2csalen)(py)$_2$] (500 mg) suspended in methanol (20 cm^3) was added powdered LiOH (500 mg), and the mixture gently refluxed with stirring for 3 h. Then a solution of lanthanum(III) nitrate hexahydrate (380 mg) in methanol (20 cm^3) was added and the mixture refluxed for 2 h. The resulting orange microcrystals were separated by filter suction, recrystallized from a large volume of absolute methanol, and dried *in vacuo*. Yield 88% (Found: C, 35.65; H, 2.35; Co, 8.95; N, 6.85. Calc. for $C_{19}H_{16}CoLaN_3O_{10}$: C, 35.45; H, 2.50; Co, 9.15; N, 6.50%).

[CoNd(csalen)(H_2O)$_2$(NO_3)]. A methanolic solution (25 cm^3) of Li_2[Co(csalen)(py)]·2.5H_2O (275 mg) and neodymium(III) nitrate hexahydrate (241 mg) was gently refluxed for 2 h. The reddish orange microcrystals thus obtained were collected by filter suction and dried *in vacuo*. Yield 87% (Found: C, 33.50; H, 2.55; Co, 8.80; N, 6.20. Calc. for $C_{18}H_{16}CoN_3NdO_{11}$: C, 33.10; H, 2.45; Co, 9.00; N, 6.45%).

[CoGd(csalen)(H_2O)(NO_3)]. This complex was obtained similarly to the Co–La complex, using gadolinium(III) nitrate hexahydrate as the metal source. Yield 90% (Found: C, 33.55; H, 2.55; Co, 9.25; N, 6.60. Calc. for $C_{18}H_{14}CoGdN_3O_{10}$: C, 33.35; H, 2.20; Co, 9.10; N, 6.50%).

Measurements.—Elemental analyses for C, H, and N were obtained from The Service Centre of Elemental Analysis, Kyushu University. Cobalt analyses were made on a Shimadzu model AA-680 atomic absorption/flame emission spectrophotometer. Infrared spectra were obtained on a JASCO IR-810 spectrometer on KBr disks or Nujol mulls. Magnetic susceptibilities of powder samples were determined by the Faraday method at room temperature. Electronic absorption spectra were recorded on a Shimadzu MPS-2000 spectrometer at room temperature in dmf or dmso. *X*-band e.s.r. spectra were recorded on a JES-FE3X spectrometer on frozen dmf solutions at liquid-nitrogen temperature. Ethylene glycol (*ca.* 10% v/v) was added to each dmf solution to make a good glassy solution. Circular dichroism spectra were recorded on a JASCO J-600C spectropolarimeter. Solutions for electronic, e.s.r. and c.d. spectral measurements were prepared under a nitrogen atmosphere to avoid oxidation of complexes by molecular oxygen. For studies of the interactions of the complexes with bases, a ten-fold excess of a base was added to a dmf solution of each complex and the mixture subjected to spectral measurements.

Results and Discussion

Synthesis and General Characterization.—The synthesis of the Co–Ln complexes was carried out by a stepwise reaction; *i.e.* the mononuclear cobalt(II) complex was isolated as [Co(H_2csalen)(py)$_2$] or Li_2[Co(csalen)(py)] and subjected to reaction with a lanthanoid(III) ion. For the synthesis of the Co–La and Co–Gd complexes, [Co(H_2csalen)(py)$_2$] was treated with La^{III} and Gd^{III}, respectively, in methanol in the presence of LiOH. For the synthesis of the Co–Nd complex, Li_2[Co(csalen)(py)] was treated with Nd^{III} in methanol. Both methods gave comparable yields and should be applicable to the synthesis of other Co–Ln complexes.

All the Co–Ln complexes are fairly stable in air in the solid state so as to allow measurement of i.r. spectra and magnetic susceptibilities. Prolonged exposure to air, however, resulted in their decomposition. In solutions the complexes are air-sensitive and decomposed into uncharacterized materials.

The i.r. spectrum of [Co(H_2csalen)(py)$_2$] showed the vibration of the free carboxyl group at 1 700 cm^{-1}. The antisymmetric stretching vibration of the carboxylate group of Li_2[Co(csalen)(py)] was found at 1 550 cm^{-1}. Similarly the carboxylate vibration of the Co–Ln complexes was observed at 1 550 cm^{-1}. The nitrate antisymmetric stretching vibration appeared as split bands at $\approx$1 440 and 1 380 cm^{-1}, suggesting bidentate co-ordination.[22] All our efforts to grow large crystals of the Co–Ln complexes suitable for *X*-ray structural analysis were in vain, but it is very likely that the lanthanoid ion is bound at the O_4 site and adopts a co-ordination number of seven or eight, with the bidentate nitrate ion and a methanol or water molecule(s) in the co-ordination sphere.

It has been shown that [Co(H_2csalen)(py)$_2$] is of high spin ($S = \frac{3}{2}$) at room temperature, though this complex exhibits a spin cross-over phenomenon at low temperature.[23] The magnetic moments (per molecule) of the Co–La, Co–Nd, and Co–Gd complexes are 2.45, 3.53, and 7.88 μ_B, respectively, at room temperature. Evidently, the cobalt(II) ion of these Co–Ln complexes is of low spin.

Electronic Spectra.—Electronic spectra of the Co–Ln complexes were measured in dmf or dmso in the region 5 000—33 000 cm^{-1}, in the absence or presence of a nitrogen-containing base. In order to examine the configuration around the cobalt(II) ion the spectra of the complexes were compared with those of related, well characterized *N,N'*-ethylenebis(salicylideneiminato)cobalt(II) [Co(salen)]. The comparisons are restricted to the region 5 000—25 000 cm^{-1}, because the ligands csalen^{4-} and salen^{2-} significantly differ from each other in electronic structure so that the electronic spectra of their complexes are ligand-dependent at >25 000 cm^{-1}. Typical spectra of the complexes are given in Figure 1.

The spectra of the complexes in dmf and dmso are essentially similar to each other and characterized by a near-i.r. band at

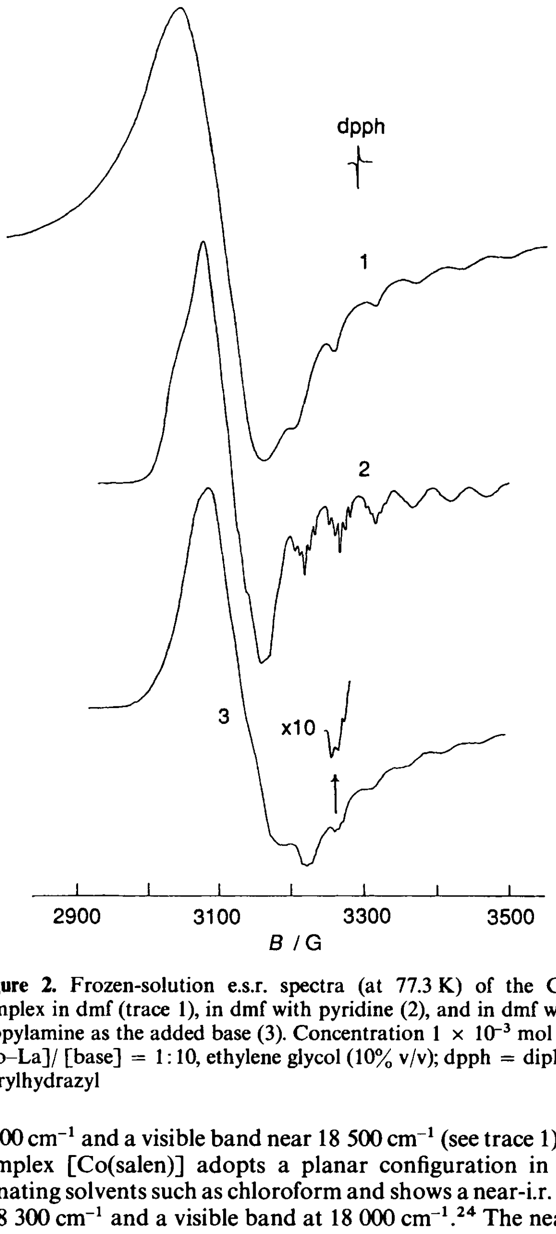


Figure 2. Frozen-solution e.s.r. spectra (at 77.3 K) of the Co–La complex in dmf (trace 1), in dmf with pyridine (2), and in dmf with n-propylamine as the added base (3). Concentration 1×10^{-3} mol dm^{-3}, [Co–La]/ [base] = 1:10, ethylene glycol (10% v/v); dpph = diphenylpicrylhydrazyl

7 300 cm^{-1} and a visible band near 18 500 cm^{-1} (see trace 1). The complex [Co(salen)] adopts a planar configuration in non-donating solvents such as chloroform and shows a near-i.r. band at 8 300 cm^{-1} and a visible band at 18 000 cm^{-1}.[24] The near-i.r. band is known to be characteristic of planar cobalt(II) complexes of salen-like Schiff bases.[25,26] A marked spectral resemblance between the Co–Ln complexes in dmf and [Co(salen)] in chloroform indicates that the former retain a planar configuration around the cobalt(II) ion in dmf and dmso. In this study we have examined the electronic spectrum of [Co(salen)] in dmf and found that it is essentially identical with that in chloroform. This suggests a low affinity of the cobalt(II) ion bound to the salen-like N_2O_2 site towards oxygen donor atoms.

In the electronic spectrum of the Co–Nd complex a fine structure appears in the region 11 000—14 000 cm^{-1} as shown in the insert of Figure 1. This can be assigned to *f–f* transitions of Nd^{III}.[27] Other *f–f* transitions which are expected to appear in the higher-frequency region are concealed by more intense *d–d*, charge-transfer, or intraligand transitions. The electronic spectrum of the Co–Gd complex is featureless and resembles that of the Co–La complex. This is quite natural because Gd^{III} shows no spin-allowed *f–f* transition.

When pyridine was added to an orange dmf solution of the Co–Ln complexes ([py]/[Co–Ln] = 10:1) the resulting deeply red solution showed a near-i.r. band at 6 600 cm^{-1} with an enhanced intensity, a discernible shoulder near 9 000 cm^{-1}, and two visible bands at ≈19 000 and ≈22 500 cm^{-1} (see trace 2). It is known that [Co(salen)] adopts a square-pyramidal configuration in pyridine with a pyridine molecule at the axial site.[28] The absorption spectrum in pyridine[29] shows two visible bands at 17 500 and 21 500 cm^{-1} and resembles trace 2 of Figure 1. The near-i.r. region of the spectrum of [Co(salen)(py)] was recorded on solid samples and two bands were observed at 6 000 and 9 000 cm^{-1}.[30] In this study we have examined the near-i.r. spectrum of [Co(salen)] in pyridine and observed a main absorption band at 5 500 cm^{-1} and a discernible shoulder near 8 000 cm^{-1}. Thus, the electronic spectra of [Co(salen)(py)] and the Co–Ln complexes in dmf containing pyridine are very similar to each other over the range 5 000—25 000 cm^{-1}, indicating that a pyridine molecule co-ordinates to the cobalt(II) centre of the Co–Ln complexes to afford a square-pyramidal configuration around the metal ion.

Trace 3 of Figure 1 is typical of the electronic spectra of the Co–Ln complexes when n-propylamine is added as a base ([NH$_2$Pr^n]/[Co–Ln] = 10:1). The pattern is on the whole very similar to that of the Co–Ln complexes with pyridine as an added base (trace 2) except for a very weak peak near 12 000 cm^{-1}. Thus, n-propylamine co-ordinates to the cobalt(II) centre of the Co–Ln complexes to afford a square-pyramidal geometry around the metal ion.

E.S.R. Spectra.—Low-spin cobalt(II) complexes may adopt a ground-state electronic structure of either $(d_{yz})^1$ or $(d_{z^2})^1$. For the cobalt(II) complexes of salen-like Schiff bases the former occurs for a planar configuration whereas the latter occurs for five- or six-co-ordinated species with a base at the apical site(s).[25,26] The two electronic structures can be readily diagnosed on the basis of e.s.r. spectra; *i.e.* the $(d_{yz})^1$ ground state affords a rhombic pattern with $g_x \gg 2.0 > g_z > g_y$ and the g_x signal has an eight-line hyperfine structure with a large hyperfine coupling constant due to the cobalt nucleus ($I = \frac{7}{2}$).[31] The $(d_{z^2})^1$ ground state affords a formally axial pattern with $g_{\parallel}$ 2.0 and $g_{\perp} > 2.0$ with a significant hyperfine structure on the $g_{\parallel}$ component.[32]

The present Co–La complex gave well resolved e.s.r. spectra on frozen solutions. The Co–Nd and Co–Gd complexes in frozen solutions gave poorly resolved spectra probably because of spin–spin interactions, and the spectra were not analysed.

Trace 1 of Figure 2 is the e.s.r. spectrum of the Co–La complex determined in frozen dmf solutions at liquid-nitrogen temperature. It shows an axial pattern with $g_{\parallel} = 2.03$ and $g_{\perp} = 2.25$, and at least seven lines of an eight-line hyperfine structure are seen on the $g_{\parallel}$ component ($A_{\parallel} = 95$ G). This is characteristic of the $(d_{z^2})^1$ ground state. Thus, a dmf molecule co-ordinates to the cobalt(II) ion at liquid-nitrogen temperature whereas this does not occur at room temperature as demonstrated above by the electronic spectral study. An essentially similar e.s.r. spectrum has been obtained on a frozen dmso solution of the Co–La complex ($g_{\parallel} = 2.01$, $g_{\perp} = 2.26$, $A_{\parallel} = 110$ G).

Trace 2 of Figure 2 is the e.s.r. spectrum of the Co–La complex when pyridine was added to a dmf solution ([py]/[Co–La] = 10:1). The spectral pattern is the same as that in dmf (trace 1) except for that the five-line superhyperfine structure due to the nitrogen nucleus ($I = 1$) is imposed on each hyperfine component of $g_{\parallel}$. The parameters obtained from the spectrum are $g_{\parallel} = 2.02$, $g_{\perp} = 2.25$, $A_{\parallel} = 90$ G, and $A_N = 13.5$ G. The result clearly demonstrates that at liquid-nitrogen temperature two pyridine molecules co-ordinate to the cobalt(II) ion to afford six-co-ordination around the metal ion, while five-co-ordination at room temperature is demonstrated by electronic spectra. 1:2 Pyridine adduct formation at liquid-nitrogen

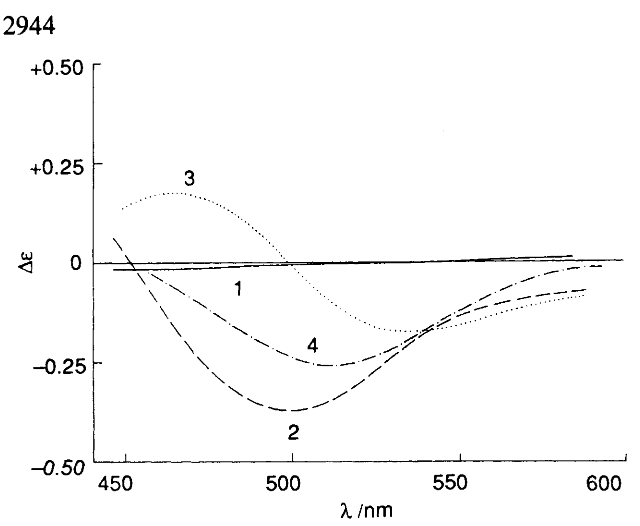


Figure 3. Circular dichroism spectra of $[Co(H_2csalen)]$ and the Co–La complex in the presence of an optically active amine (ten-fold excess over Co^{II}) in dmf. Traces: 1, $[Co(H_2csalen)]$–(*S*)-2-aminobutane; 2, Co–La–(*S*)-2-amino-1-propanol; 3, Co–La–(*S*)-2-aminobutane; 4, $[Co(H_2csalen)]$–(*S*)-2-amino-1-propanol

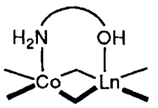
temperature occurs also in the case of [Co(salen)].[31] Similar e.s.r. spectra with a five-line superhyperfine structure were obtained when *o*-, *m*-, or *p*-toluidine was adopted as a base.

Trace 3 is the e.s.r. spectrum when n-propylamine was added to a dmf solution of the Co–La complex ($[NH_2Pr^n]/[Co–La]$ = 10:1). The pattern is again of the $(d_{z^2})^1$ configuration but the superhyperfine structure imposed on each hyperfine component of $g_{\parallel}$ consists of three lines in this case. Similar spectra with a three-line superhyperfine structure were obtained when other aliphatic amines and aminoalcohols were adopted as the base.

The above e.s.r. spectral results indicate that pyridine and its derivatives have a high affinity compared with aliphatic amines for the cobalt(II) ion of the Co–Ln complexes, affording six-co-ordination around the metal ion.

Specific Binding of Aminoalcohols at the Co–Ln *Centre*.—In the previous study on the Cu–Ln homologues we found that substrates with a N- and an O-donor group are specifically bound at the Cu–Ln centre, forming a bond with the copper ion at the N-donor atom and with the lanthanoid ion at the O-donor atom.[18] In this study we have examined whether a similar specific binding of substrates occurs at the Co–Ln centre, using the Co–La complex as a host and 2-aminoethanol and a related chiral aminoalcohol (*S*)-1-amino-2-propanol as substrates. The co-ordination of these bases to the cobalt(II) ion *via* the nitrogen has been evidenced by electronic spectra as discussed above.

First we examined c.d. spectra of the mononuclear cobalt(II) complex $[Co(H_2csalen)]$ in dmf containing (*S*)-2-aminobutane (*ca.* ten-fold excess over Co^{II}) as base (Figure 3, trace 1). No band in the visible region occurs because the amine co-ordinated to the cobalt(II) ion can rotate about the Co–N bond and hence the chiral residue gives rise to little vicinal effect to the cobalt(II) ion. When the Co–La complex was adopted as a host and (*S*)-2-amino-1-propanol as a substrate a fairly strong c.d. band appeared in the visible region (trace 2). This is an indication that the aminoalcohol is bound to the Co–Ln centre, through the amino nitrogen to the Co^{II} and through the hydroxy oxygen to the La^{III} so that the ethylene conformation is fixed as δ or λ.



Some confusing results were obtained (*i*) when (*S*)-2-aminobutane was added to a dmf solution of the Co–La complex (trace 3) and (*ii*) when (*S*)-2-amino-1-propanol was added to a dmf solution of $[Co(H_2csalen)]$ (trace 4). One might expect only a weak c.d. in both cases so long as free rotation of the base about the Co–N bond is possible, but a significant optical activity was induced in the visible region in both cases. Therefore, it is most plausible that rotation of the chiral substrate bound to the cobalt(II) ion is hindered probably because of some intramolecular non-covalent interactions. In case (*i*) the (*S*)-2-aminobutane bound to the cobalt(II) ion must be fixed with respect to the Co–N bond owing to a pronounced steric effect from the dmf molecules co-ordinated to the lanthanum(III) centre. This situation is similar to the enhanced stereoselectivity in tris(1,3-diketonato)lanthanoid complexes of a chiral 1,3-diketone when dissolved in donor solvents.[33] The lanthanoid complexes form an adduct by ligation of some solvent molecules and this gives rise to an increased interligand interaction within the complex molecule and thence enhanced stereoselectivity with respect to the configuration about the lanthanoid ion. In case (*ii*) the hydroxy group of the (*S*)-2-amino-1-propanol, bound at the cobalt centre through the nitrogen atom, may be involved in hydrogen bonding with the oxygen atoms of the O_4 co-ordination site. A similar hydrogen bonding has been suggested for $[Co(H_2csalen)(H_2O)_2]$.[21]

Thus, we may conclude that ethanolamine and related aminoalcohols can be bound at the Co–La centre as shown.

Acknowledgements

This study was partly supported by a Grant-in-aid for Scientific Research from the Ministry of Education, Science and Culture (No. 62430011).

References

1 See, for example, S. Gambarotta, A. Arena, C. Floriani, and P. F. Zanazzi, *J. Am. Chem. Soc.*, 1982, **104**, 5082; F. Arena, C. Floriani, A. Chiesi-Villa, and C. Guastini, *Inorg. Chem.*, 1986, **25**, 4589.
2 J. S. R. Richardson, K. A. Thomas, B. H. Rubin, and D. C. Richardson, *Proc. Natl. Acad. Sci. USA*, 1976, **73**, 2206.
3 See, for example, G. Palmer, G. T. Babcock, and L. E. Vickery, *Proc. Natl. Acad. Sci. USA*, 1976, **73**, 2206.
4 O. Kahn, *Struct. Bonding* (*Berlin*), 1987, **68**, 89.
5 U. Casellato, P. A. Vigato, and M. Vidali, *Coord. Chem. Rev.*, 1977, **23**, 31.
6 D. E. Fenton, U. Casellato, P. A. Vigato, and M. Vidali, *Inorg. Chim. Acta*, 1982, **62**, 57.
7 P. Zanello, S. Tamburini, P. A. Vigato, and G. A. Mazzocchin, *Coord. Chem. Rev.*, 1987, **77**, 165.
8 M. Tanaka, H. Ōkawa, I. Hanaoka, and S. Kida, *Chem. Lett.*, 1974, 71; M. Tanaka, M. Kitaoka, H. Ōkawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2469.
9 H. Ōkawa, Y. Nishida, M. Tanaka, and S. Kida, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 127.
10 N. Torihara, H. Ōkawa, and S. Kida, *Inorg. Chim. Acta*, 1976, **26**, 97; *Chem. Lett.*, 1978, 185, 1269.
11 M. Mikuriya, H. Ōkawa, S. Kida, and I. Ueda, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2920.
12 N. Torihara, H. Okawa, and S. Kida, *Chem. Lett.*, 1979, 683.
13 H. Ōkawa, W. Kanda, and S. Kida, *Chem. Lett.*, 1980, 1281.
14 I. Morgenstern-Badarau, M. Rerat, O. Kahn, J. Jaud, and J. Galy, *Inorg. Chem.*, 1982, **21**, 3050; S. Desjardins, I. Morgensterm-Badarau, and O. Kahn, *ibid.*, 1984, **23**, 3833.
15 Y. Journaux, O. Kahn, J. Zarembowitch, J. Galy, and J. Jaud, *J. Am. Chem. Soc.*, 1983, **105**, 7585.
16 M. Sakamoto, M. Takagi, T. Ishimori, and H. Ōkawa, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 1613.
17 J. P. Veale, J. A. Cunningham, and D. J. Phillips, *Inorg. Chim. Acta*, 1979, **33**, 113.
18 M. Sakamoto, T. Ishimori, and H. Ōkawa, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 3319.

19 J. C. Duff and E. J. Bills, *J. Chem. Soc.*, 1932, 1987.

20 N. Torihara, H. Ōkawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3236.

21 J. Zarembowitch, R. Claude, and O. Kahn, *Inorg. Chem.*, 1985, **24**, 1576.

22 K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' 2nd edn., Wiley, New York, 1970, p. 171.

23 P. Threry and J. Zarembowitch, *Inorg. Chem.*, 1986, **25**, 2001 and refs. therein.

24 H. Nishikawa and S. Yamada, *Bull. Chem. Soc. Jpn.*, 1964, **37**, 8; S. Yamada, *Coord. Chem. Rev.*, 1966, **1**, 415.

25 Y. Nishida and S. Kida, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 461; 1978, **51**, 143.

26 Y. Nishida and S. Kida, *Chem. Lett.*, 1973, 57; *Coord. Chem. Rev.*, 1979, **27**, 275.

27 G. H. Dieke, 'Spectra and Energy Levels of Rare Earth Ions in Crystals,' Interscience, New York, 1968.

28 E. Cesarotti, M. Gullotti, A. Pasini, and R. Ugo, *J. Chem. Soc., Dalton Trans.*, 1977, 757.

29 K. Nakamoto, H. Oshio, H. Ōkawa, W. Kanda, K. Horiuchi, and S. Kida, *Inorg. Chim. Acta*, 1985, **108**, 231.

30 M. A. Hitchman, *Inorg. Chem.*, 1977, **16**, 1985.

31 E. Ochiai, *J. Inorg. Nucl. Chem.*, 1973, **35**, 1727.

32 R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, 1979, **79**, 139.

33 H. G. Brittain, *J. Chem. Soc., Dalton Trans.*, 1982, 2059; *Polyhedron*, 1983, **2**, 261; *J. Chem. Soc., Dalton Trans.*, 1983, 1165.

Received 12*th April* 1990; *Paper* 0/01659D