Pergamon

Polyhedron Vol. 14, No. 2, pp. 223–229, 1995

0277–5387/95 \$9.50+0.00

0277–5387(94)00245–2

A NEW ISOMER OF THE *CIS*-[Co(CYCLEN)Cl_2]$^+$ CATION (CYCLEN = 1,4,7,10-TETRAAZACYCLODODECANE)

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(*Received* 16 *April* 1994, *accepted* 6 *June* 1994)

Abstract—This work describes the preparation of a new complex, **1**, and its perchlorate salt **2** when cyclen (1,4,7,10-tetraazacyclododecane) and $CoCl_2 \cdot 6H_2O$ are reacted in anhydrous methanol. ^1H and ^{13}C NMR spectroscopies were used to determine the absolute configuration of the new coordination compound.

Complexes containing macrocyclic ligands have the possibility of forming a wide range of isomers both geometrical and conformational and can therefore provide a series of compounds suitable for the study of some of the factors that affect the reactivity of a particular complex. In 1966 the reaction between cobalt chloride and 1,4,7,10–tetraazacyclododecane (cyclen) was first reported[1] and it was suggested at that time a *cis* configuration for the chloro ligands in the complex. Later, the structures of the *cis*-dinitro[2] and carbonato[3] complexes were further studied by X-ray crystallography, but it was not until 1985 that the absolute configuration of the protons on the secondary nitrogens of the dichloro species was determined by ^1H NMR spectroscopy.[4] This compound was shown to have the *syn,anti-cis* configuration.

When $CoCl_2 \cdot 6H_2O$ was reacted with cyclen, we obtained a blue–violet solid besides the previously described compound. It was then of interest to characterize fully the new compound from this reaction. In this paper we report the preparation and characterization of the *syn,syn-cis*-dichloro(cyclen) cobalt(III) cation.

EXPERIMENTAL

Preparations

The ligand 1,4,7,10-tetraazacyclododecane tetrahydrochloride (cyclen · 4HCl) was prepared as reported before.[5,6] The elemental analysis for $C_8H_{24}N_4Cl_4$ requires C, 30.2; H, 7.6; N, 17.6; Cl, 44.6; Found C, 30.5; H, 7.8; N, 17.8; Cl, 43.8%.

Syn,anti-cis-*dichloro*(*cyclen*)*cobalt*(III) *perchlorate*. This compound was prepared as reported previously.[4] (Found: C, 24.3; H, 5.0; N, 13.6. $C_8H_{20}N_4Cl_3O_4Co$ requires C, 23.9; H, 5.0; N, 13.9%.)

Syn,syn-cis-*dichloro*(*cyclen*)*cobalt*(III), syn,anti-cis-*di-chloro*(*cyclen*)*cobalt*(III) *tetrachlorocobaltate*(II), **1**. LiOH (0.1198 g, 4.99 mmol) was warmed in 20 cm^3 of anhydrous methanol. Undissolved lithium hydroxide was separated from the solution and discarded. Cyclen · 4HCl (0.50 g, 1.57 mmol) was added to this solution and when completely dissolved, $CoCl_2 \cdot 6H_2O$ (0.375 g, 1.57 mmol) in 20 cm^3 of methanol was added. Air was bubbled through the solution for half an hour. The first dark blue–violet solid formed was filtered off and washed with methanol. Yield (0.3293 g) (Found: C, 24.1; H, 5.1; N, 13.6; Cl, 34.8. $C_{16}H_{40}N_8Cl_8Co_3$ requires C, 23.9; H, 5.0; N, 13.9; Cl, 35.2%.)

Syn,syn-cis-*dichloro*(1,4,7,10-*cyclen*)*cobalt*(III) *and* syn,anti-cis-*dichloro*(1,4,7,10-*cyclen*)*cobalt*(III) *perchlorates*, **2**. **1** was dissolved in a very small amount of cold water and stirred vigorously until all the complex had dissolved, then $\approx$ 2 cm^3 of 3 M $HClO_4$ were added. After about a minute the mixture of perchlorates started to crystallize out. Then, this was frozen, and allowed to thaw at room temperature, the solid was filtered off, washed with iced cold 0.3 M $HClO_4$ and then with ethanol, and finally

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air dried, **2**. (Found: C, 23.8; H, 5.0; N, 13.8; Cl, 26.7. $C_8H_{20}N_4Cl_3O_4Co$ requires C, 23.9; H, 5.0; N, 13.9; Cl, 26.5%.)

Proton NMR experiments

The dried tetrachlorocobaltate and perchlorate salts were dissolved in [$^2H_6$] dimethyl sulphoxide and their ^{1}H and ^{13}C NMR spectra were recorded using Varian VXR 200S and Varian VXR 300S spectrometers using TMS as internal standard.

RESULTS AND DISCUSSION

It has been observed that tetraaza macrocyclic ligands stabilize *cis* and *trans* isomers when coordinated to transition metal ions in octahedral complexes containing halides in the coordination sphere. Several diasteroisomers have been isolated for the *trans*-dichloro cyclam and cobalt, namely the RSSR[7] and the RRRR(SSSS).[8] It has also been found that small changes in the conformation of the macrocyclic ligand can stabilize different conformers for the same *trans*-RSSR configuration.[9] However, in the case of the dichloro cobalt salt and cyclen only the *cis* isomer has been isolated. This has been explained in terms of the size of the cavity of the macrocyclic ligand. The results of this work suggest that we have isolated a different isomer from the *syn,anti-cis* previously obtained, namely the *syn,syn-cis* isomer.

Some attempts were made to grow a single crystal of **1**, however, the compound precipitated as flakes. Thus, in order to determine its absolute configuration, ^{1}H and ^{13}C NMR spectroscopies were employed.

NMR characterization of [$^2H_6$]dimethyl sulphoxide solutions of this type of complexes have shown that they are inert towards ligand substitution and isomerization. It is worthwhile to mention that the configuration assigned to these complexes through the NMR studies agrees with that provided by X-ray crystallography.[10] Besides, there is also kinetic evidence about the inertness towards ligand substitution of the *cis*-[Co(cyclam)Cl_2]$^+$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) in [$^2H_6$]-dimethylsulphoxide solutions, where it was

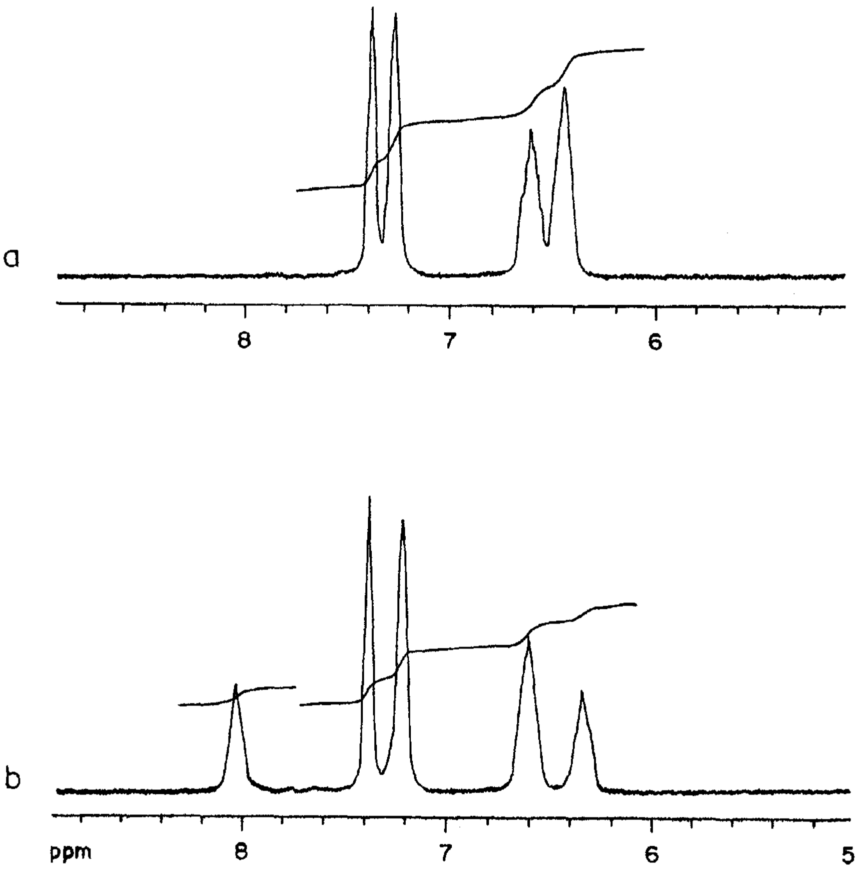

Fig. 1. ^{1}H NMR spectra of (a) 50% mixture of the *syn,syn-cis* and *syn,anti-cis*-[Co(cyclen)Cl_2]ClO_4 with (b) lithium chloride.

proved that chloride is not exchanged by dimethylsulphoxide.[13] This type of behaviour was also observed for the *syn,anti-cis*-[Co(cyclen)Cl$_2$]$^+$ cation.[14] Electrical conductivity measurements of dimethylsulphoxide solutions of compounds **1** and **2** also support the fact that these complexes are inert towards ligand substitution, $\Lambda_M = 88$ ohm^{-1} cm^2 mol^{-1} for the *syn,syn-cis*-dichloro (cyclen)cobalt(III), *syn,anti-cis*-dichloro(cyclen) cobalt(III) tetrachlorocobaltate(II), **1**, while for **2** $\Lambda_M = 40.75$ ohm^{-1}cm^{2}mol^{-1}, corresponding to 2:1 and 1:1 electrolytes, respectively.[15]

The ^{1}H NMR spectrum of **2** in [^{2}H$_6$]dimethyl sulphoxide shows, apart from the multiplet due to the CH$_2$ protons between δ 2.2 and 3.6, four broad peaks of equal area at δ 6.44 (2 H), 6.60 (2 H), 7.25 (2 H), and 7.40 (2 H), which are assigned to the amine protons (Fig. 1a). This is consistent with an equimolecular mixture of either (I) and (III), or (II) and (III) (Fig. 2). In the first case, the mixture would be formed by the compound that has two protons *trans* to Cl pointing away from each other (*syn,syn*) and the (*syn,anti*) isomer, or in the second case, a mixture composed by the compound containing two protons pointing towards each other (*anti,anti*), a structure analogous to that of the known complex *cis*-RRRR(SSSS)-[Co(cyclam)Cl$_2$] Cl[11] and the (*syn,anti*) compound. Addition of an excess of lithium chloride to the solution of dimethylsulphoxide, causes a shift of several peaks. The new set of peaks is at δ 6.32, 6.60, 7.25, 7.40 and 8.05 ppm (Fig. 1b). From a closer inspection of the area and the form of the peaks, those at δ 6.32 (1 H), 7.25 (2 H) and 8.05 (1 H) can be assigned to the *syn,anti* isomer, already reported. The downfield shift of one peak in the presence of chloride is due to hydrogen bonding in the chloride ion pair and, assuming that the chloride anion prefers a site as far from the coordinated chlorides as possible, this identifies the protons at δ 7.25 as those on the mutually *trans* nitrogens, that at δ 6.32 as the *syn* proton and the other at δ 8.05 as the *anti* proton, as it has been shown in the past.[11] On the other hand, the peaks of the same area, i.e. two protons, at 6.60 and 7.40 do not show any shift after the addition of lithium chloride, therefore, these signals can be assigned to the *syn,syn* isomer, since chloride does not interact with these protons. It has also been shown for the *anti,anti-cis*-dichloro cyclam cobalt derivative that on addition of an excess of lithium chloride one of the two peaks is downfield shifted.[13]

The ^{1}H NMR spectrum of **1** in [^{2}H$_6$]dimethyl sulphoxide shows the multiplet due to the CH$_2$ protons between δ 2.2 and 3.6 and five signals at δ 6.40 (1 H), 6.60 (2 H), 7.15 and 7.25 (3 H) and 7.40 (2 H) (Fig. 3a), which are assigned to the amine protons. This is consistent with a mixture of either

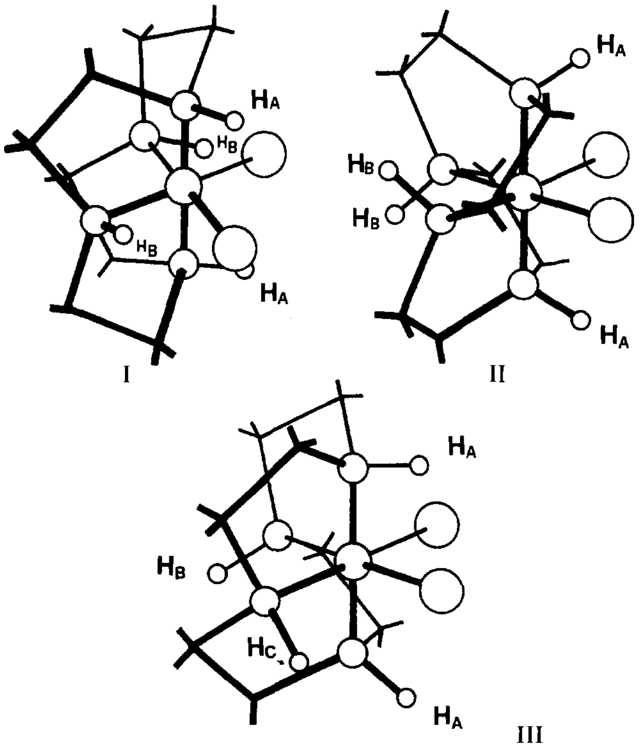

Fig. 2. (I) (*syn,syn*), (II) (*anti,anti*) and (III) (*syn,anti*) isomers.

(I) and (III), or (II) and (III) isomers. Addition of lithium chloride to the solution of **1** in dimethylsulphoxide causes a shift of several peaks, and the new amine peaks are situated at $\delta = 6.30$ (1 H), 6.60 (2 H), 7.20 (2 H), 7.35(2 H) and 8.15 (1 H) (Fig. 3b). The peaks at 6.30, 7.20 and 8.15 can be assigned to the already found *syn,anti-cis* isomer, whereas the peaks at $\delta = 6.60$ and 7.35 ppm can be assigned to the *syn,syn-cis* isomer, since these signals are not sensitive to the addition of an excess of lithium chloride. Provided that the areas under the peaks at 6.60 and 7.35 are smaller than the area under the peak at 7.20 (2 H) we conclude that this compound does not contain an equimolecular amount of the *syn,syn-cis* and *syn,anti-cis* isomers, but the tetrachlorocobaltate salt is composed by 78% of the *syn,anti-cis* isomer and 22% of the *syn,syn-cis* isomer.

When the tetrachlorocobaltate salt is dissolved in water, and perchloric acid added, a mixture of perchlorates, 50% of *syn,syn-cis* and 50% of *syn,syn-cis* isomers is recovered. It is worthwhile to point out that the absolute configuration of the isomers did not change when compared with the tetrachlorocobaltate salt. However the difference in proportions can be explained in terms of a possible faster hydrolysis of the *syn,anti-cis* isomer.

The ^{13}C NMR spectrum of the tetrachlorohydrate salt of cyclen in [$^2H_6$] dimethylsulphoxide shows a single peak at 43.467 ppm, indicating that all the carbon atoms in the molecule are equivalent.

The ^{13}C NMR spectrum of the *syn,anti-cis*-[Co(cyclen)Cl_2]ClO_4 (Fig. 4a) shows four peaks of approximately the same intensity at δ 46.234, 49.886, 54.229 and 57.388. Addition of an excess of lithium chloride to the dimethylsulphoxide solution causes a small shift of the peak originally at 49.886 ppm to high field (49.678) (Fig. 4b). This peak can be assigned to the closest carbon atom to the *anti*

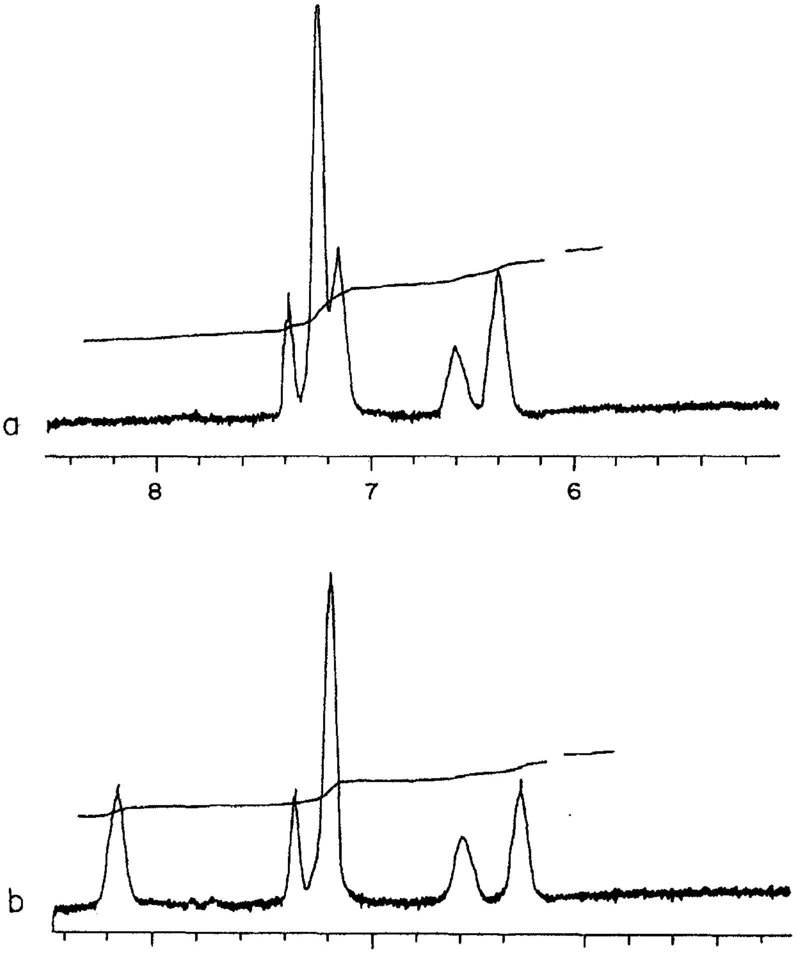

Fig. 3. ^1H NMR spectra of (a) 78% mixture of *syn,syn-cis*- and *syn,anti-cis*-[Co(Cyclen)Cl_2]$CoCl_4$ and (b) with lithium chloride.

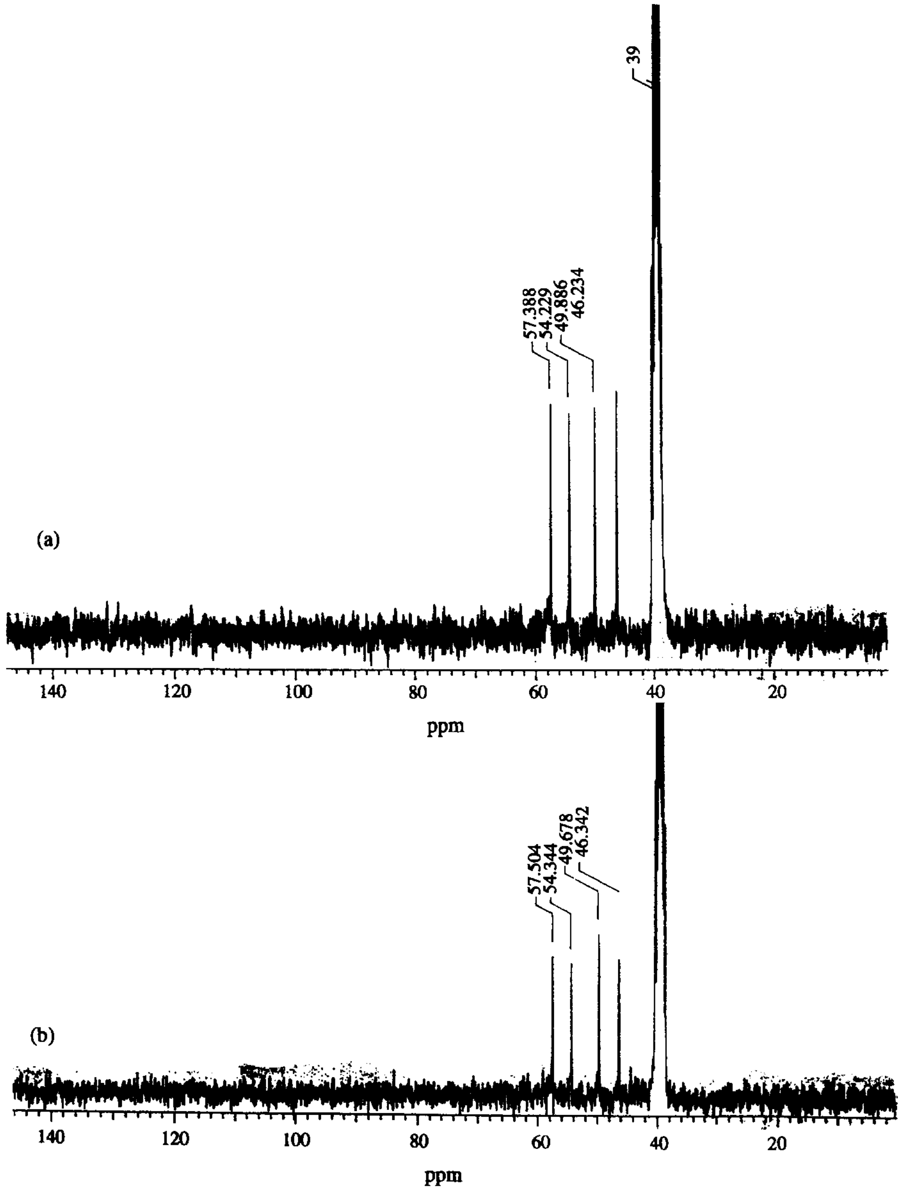

Fig. 4. ^{13}C NMR spectra of (a) (III) *syn,anti-cis*-$[Co(cyclen)Cl_2]ClO_4$ and (b) with lithium chloride.

N—H group, since the addition of Cl^- to sample causes the formation of a hydrogen bond with the H on this N atom and interacts with the H on the closest C atom as shown in Fig. 5 (C).

The ^{13}C NMR spectrum of **2**, the *syn,syn-cis* 50% and *syn,anti-cis* 50% perchlorates mixture shows peaks at 46.255, 49.712, 49.866, 54.247, 57.402 and 57.742 of different intensities (Fig. 6a). The four peaks at 57.402, 54.247, 49.866 and 46.255 are approximately 0.75 of the height of those at 57.742 and 49.712. The four peaks of the same intensity can be assigned to the carbon atoms of the *syn,anti-cis* isomer, whereas the other two peaks correspond to the *syn,syn-cis* isomer. The addition of an excess

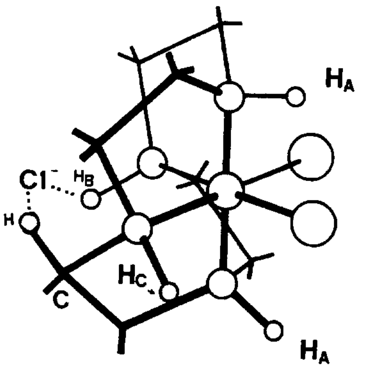

Fig. 5. Ion pair showing the interaction between the chloride ion and the *anti* N—H as well as the C—H.

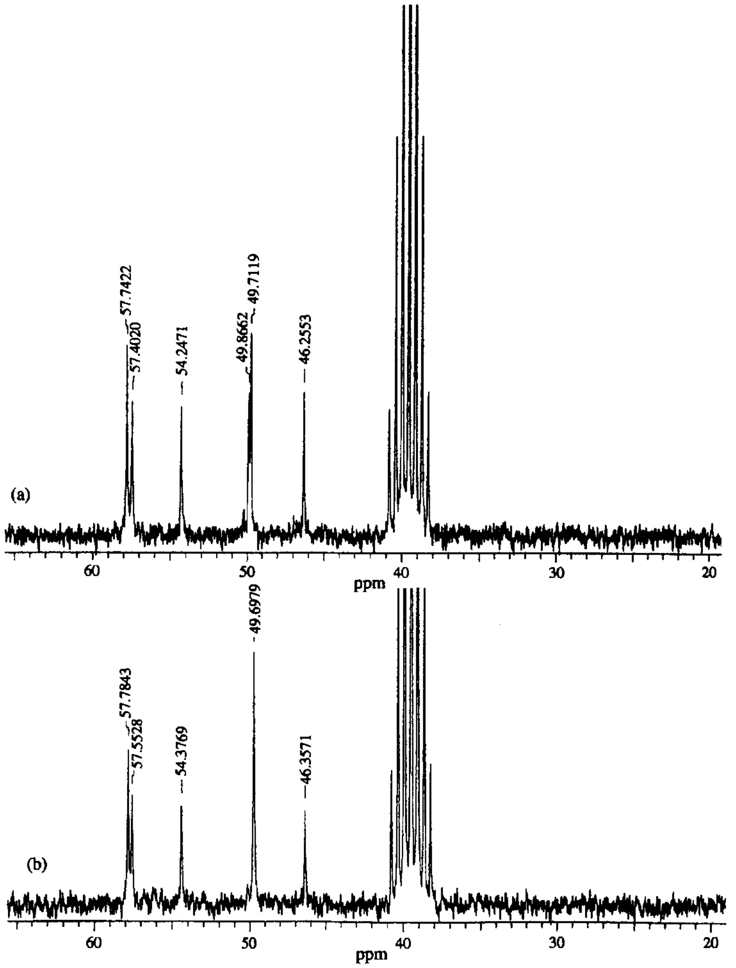

Fig. 6. ^{13}C NMR spectra of (a) 50% mixture of the (I) *syn,syn-cis*- and (III) *syn,anti-cis*-[Co(cyclen)Cl$_2$]ClO$_4$ and (b) with lithium chloride.

of lithium chloride to the solution causes a shift of the peak originally at 49.866 to high field, merging the original peaks at 49.866 and 49.712 into one at 49.698 (Fig. 6b) of about three times the intensity of the former one. It can therefore be concluded that the peak that shifts to high field in the *syn,anti-cis* isomer as well as the peak at 49.866 of **2** can be assigned to the carbon atom closest to the N—H group, since the addition of Cl$^-$ to the sample must form a hydrogen bond with the H on the nitrogen and also with the H on this carbon atom. It can be concluded that we have isolated a different isomer from the previously reported, namely the *syn,syn-cis* isomer, which has two sets of equivalent carbons, while the *syn,anti-cis* has four. This supports the fact that the *syn,syn-cis* isomer is more symmetric.

The ^{13}C NMR spectrum of **1** has six peaks at 57.963, 57.501, 54.549, 50.245, 49.806 and 46.893 ppm, being the peaks at 57.963 and 50.245 about double in intensity with respect to the other four. This spectrum can not be as straightforwardly interpreted as the others above; particularly, since a very concentrated solution was required to carry out the experiment. Under these conditions the intermolecular and intramolecular interactions increase due to the presence of the tetrachlorocobaltate ion. As the ^{1}H NMR spectrum of the concentrated sample shows strong interactions in the N—H region, any shift associated with ion pairs formation could be ambiguous.

Acknowledgements—We wish to thank M. C. Federico Del Río for the recording of the ^{1}H NMR spectra at the Instituto de Química, UNAM, and Mr. Ricardo Acosta for his assistance with the drawings. We also wish to thank the financial support to DGAPA-UNAM (Research project IN102989).

REFERENCES

1. J. P. Collman and P. W. Schneider, *Inorg. Chem.* 1966, **5**, 1380.

2. Y. Itaka, M. Shina and Kimura, *Inorg. Chem.* 1974, **13**, 2886.
3. J. H. Loehlin and E. B. Fleischer, *Acta C. Sect. B* 1976, **32**, 3063.
4. M. E. Sosa and M. L. Tobe, *J. Chem. Soc., Dalton Trans.* 1985, 475.
5. J. P. Collman and P. W. Schneider, *Inorg. Chem.* 1966, **5**, 1380.
6. J. E. Richman and T. J. Atkins, *J. Am. Chem. Soc.* 1974, **96**, 2268.
7. (a) B. Bosnich, C. K. Poon and M. L. Tobe, *Inorg. Chem.* 1965, **4**, 1102. (b) M. E. Sosa-Torres, M. J. Rosales and R. A. Toscano, to be published.
8. C. J. Cooksey and M. L. Tobe, *Inorg. Chem.* 1978, **17**, 1558.
9. L. M. Flores-Vélez, J. Sosa-Rivadeneyra, M. E. Sosa-Torres, M. Rosales-Hoz and R. A. Toscano, *J. Chem. Soc., Dalton Trans.* 1991, 3243.
10. E. Ahmed, C. Chaterjee, C. J. Cooksey, M. L. Tobe, G. Williams and M. Humanes, *J. Chem. Soc., Dalton Trans.* 1989, 645.
11. P. O. Whimp, M. F. Bailey and N. F. Curtis, *J. Chem. Soc. A*1 1970, 1956.
12. H. Nakazawa, U. Sakaguchi, H. Yoneda and Y. Morimoto, *Inorg. Chem.* 1981, **20**, 1973.
13. J. Lichtig, M. E. Sosa and M. L. Tobe, *J. Chem. Soc., Dalton Trans.* 1984, 581.
14. S. E. Castillo-Blum, M. Sacristán-Fanjul and M. E. Sosa-Torres, to be published.
15. W. J. Geary, *Coord. Chem. Rev.* 1971, **7**, 81.