Inorganica Chimica Acta, *178* (1990) 9–12

Inorganica Chimica Acta

LETTER

Towards the Periodic Table of metallocorrolates: synthesis and characterization of main group metal complexes of octamethylcorrole

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(Received September 26, 1990)

The existence in nature of complexes with tetrapyrrolic macrocyclic ligands different from the porphyrin, such as the vitamin B12 coenzyme, has generated great interest in their chemistry. The ability of these macrocycles to carry out several reactions and their possible applications in catalysis has been the object of many investigations [1].

In the last few years our attention has been focused on corrole, a tetrapyrrolic macrocycle which can be considered as intermediate in structure between porphyrin and corrin.

In fact, it has a corrin-like molecular skeleton, with a direct link between two pyrrole rings, but still retains an aromatic 18-electrons π system similar to that of porphyrin.

In a previous paper [2] we reported the synthesis of several transition metal complexes of corrole and established three efficient and reproducible routes to metallo-corrolates.

An NMR study on the paramagnetic Fe(III) derivative [3] gave several informations on its electronic state and ligand binding properties in solution and evidentiated some differences in the ligand field effects between corrole and porphyrin.

These different properties can probably be ascribed to the different size of the coordination 'hole' accessible to metal ions in the complexes of the two macrocycles [4]. Although corrole seems to have a more rigid structure than porphyrin, this ligand is capable of chelating a variety of transition metals without significant distortion of the macrocycle plane as confirmed by an X-ray crystal structure determination that has been performed on a Rh(III) complex [2].

Our interest in the chemistry of corrole complexes has led us to undertake an investigation on the chelating ability of this macrocycle toward different metal ions.

In this paper we describe the synthesis and characterization of some corrolato complexes of main group metals.

Experimental

^{1}H NMR spectra were recorded on Bruker WP 80 SY and Bruker AM 400 instruments as $CDCl_3$ solutions. All chemical shifts are given in ppm from tetramethylsilane (TMS) and were referenced against the solvent residual signal. IR spectra were measured with a Perkin-Elmer model 983 spectrophotometer as Nujol mulls and electronic spectra on a Jasco model 7850 spectrophotometer. 1,19-dideoxy-2,3,7,8,12,13,17,18-octamethylbiladiene-*ac* dihydrobromide (BD) as well as 2,3,7,8,11,12,13,17,18-octamethylcorrole (H_3OMC) were prepared following the procedure previously reported [2]. All solvents (Farmitalia) were reagent grade and were used without further purification.

Reaction of 1,19-dideoxy-2,3,7,8,12,13,17,18-octamethylbiladiene-ac dihydrobromide with metal salts

Biladiene (500 mg) and sodium acetate (1 g) were dissolved in methanol (100 cc) and the stoicheiometric amount of the appropriate metal salt was added while stirring. The resulting green solution was refluxed for 6 h. The solvent was then evaporated and the residue extracted with THF. When $SnCl_2$ or $GeCl_4$ were used, the filtrate was purified by column chromatography on silica gel (eluant: choroform). Yields: 60% (Sn), 40% (Ge).

With $InCl_3$ we obtained an analytical pure product after several crystallizations from THF/n-pentane 1:3. Purification by column chromatography on different absorbants (silica gel, alumina or Florisil) caused extensive decomposition of the complex. Yield: 12%.

Reactions of corrole

Synthesis of [InOMC]

H_3OMC (500 mg) was dissolved in DMF (100 cc) together with the stoicheiometric amount of $InCl_3$ and refluxed, under nitrogen, for 10 min. The solvent was vacuum evaporated and the residue was treated as above. Yield: 15%.

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0020-1693/90/$3.50

Synthesis of {[ZnOMC]$^-$[PyH]$^+$}

H_3OMC (500 mg) was dissolved in pyridine (50 cc) and the stoicheiometric amount of Zn(OAc)$_2$ was added. The mixture was refluxed for 5 min, then cooled to room temperature and n-hexane (100 cc) was added. The first precipitate of unreacted Zn(OAC)$_2$ was filtered and the solution was cooled at 0 °C. Crystals of the product separated after 12 h. Yield: 20%.

All the compounds gave satisfactory elemental analysis. Spectral properties are reported in Table 1.

Results and discussion

The synthesis of metallo-corrolates can be achieved either by cyclization of the linear tetra-pyrrolic precursor, 1,19-dideoxy-biladiene-*ac*, in the presence of metal salts, or by reacting the preformed macrocycle with different metal carriers.

We have now applied such procedures to main group metals (Sn, Ge, In) and to Zn, thus testing the ability of corrole to coordinate metals with different oxidation states.

We have thus obtained {[ZnOMC]$^-$[PyH]$^+$}, [SnOMCX], [GeOMCX] (X = Cl$^-$ or CH$_3$COO$^-$) and [InOMC] that represent the first examples of non-transition metal corrolates.

The first synthetic method followed has been the cyclization of BD: this synthesis is carried out in a methanolic solution in the presence of an excess of sodium acetate. The presence of a base is necessary for the formation of the green biladiene free base, which is the first step of the cyclization [5].

The success of the reaction is strongly dependent on the metal ion: thus Sn(IV) and Ge(IV) corrolates are formed in very good yields while In(III) gives lower yields.

Tin corrolate has been obtained using SnCl$_2$ as starting material. During the metalation reaction Sn(II) is oxidized to Sn(IV) to give [Sn(OMC)X].

The nature of the counterion in the resulting complex depends on the synthetic conditions. If NaOAc is used as base, we obtained [Sn(OMC)OAc] with a trace amount of [Sn(OMC)Cl], but if NEt$_3$ is employed, the product is [Sn(OMC)Cl].

The 80 MHz ^{1}H NMR spectra of these complexes are strongly dependent on the counterion: in fact in the case of the chloride derivative the *meso*-protons of the macrocycle appear as two signals at 10.22 (5,15-H) and 10.00 (10-H) ppm, whilst in the spectrum of the acetate only one signal appears at 10.56 ppm.

These results are probably due to the different coordination geometry in the two complexes. The acetate ion in fact behaves as a bidentate ligand as confirmed by the IR spectrum of the complex

TABLE 1. Spectral data of metallo-corrolates

Complex	IR (cm^{-1})[a]	λ_{max} (nm)[b]	$\Delta H/H°$ (ppm)[c]
Sn(OMC)OAc	1560(νC=O)	574; 537; 406	10.56(s,3H); 3.74(s,3H); −1.36(s,3H)
			10.22(s,2H); 10.00(s,1H); 3.80(s,6H); 3.75(s,18H); −1.40(s,3H)[d]
Sn(OMC)Cl	268(νSn–Cl)	566; 532; 409	10.10(s,2H); 9.92(s,1H); 3.95(s,6H); 3.75(s,18H)
Sn(OMC)OH		578; 543; 410	10.08(s,3H); 3.64(s,24H); −3.72(s,1H)
Ge(OMC)OAc	1572(νC=O)	560; 524; 403	9.75(s,3H); 3.78(s,6H); 3.63(s,6H); 3.58(s,6H); −1.35(s,3H)
Ge(OMC)Cl	284(νGe–Cl)	569; 533; 401	9.74(s,2H); 9.66(s,1H); 3.83(s,6H); 3.61(s,18H)
In(OMC)		577; 539; 409	10.32(s,3H); 3.70(s,24H)
{[Zn(OMC)]$^-$[PyH]$^+$}		575; 539; 409	10.04(s,2H); 9.98(s,1H); 3.63(s,18H); 3.52(s,6H) 7.12–6.68(br,6H)

[a] Nujol mulls. [b] CHCl$_3$ solutions. [c] CDCl$_3$ solutions, 80 MHz spectra. [d] CDCl$_3$ solutions, 400 MHz spectra.

(ν(C=O) = 1560 cm^{-1}) [6] which probably has the structure represented in Fig. 1.

The distortion introduced in the macrocycle, which can be planar or ruffled, destroys the classical N–S symmetry of corrole and leads to coalescence of the resonances due to the *meso*-protons. In the 400 MHz ^{1}H NMR spectrum of [Sn(OMC)OAc], however, the two different resonances are resolved thus demonstrating that the pattern observed at 80 MHz is generated by superimposition of the signals.

No difference has been observed in the 80 or 400 MHz ^{1}H NMR spectra of [Sn(OMC)Cl].

The affinity of Sn corrolate towards different counterions is opposite to that of Sn porphyrinate: with this latter ligand in fact the favourite product is [$SnPCl_2$] [7]. This is not surprising considering the different 'hole' size of the two macrocycles. Sn complexes with porphyrines are reported to be those [8] where the major radial expansion of the macrocycle core occurs. The acetate, behaving as a bidentate ligand, pushes the tin atom out of the plane of the corrole and decreases the steric constraint due to coordination. The smaller size of the coordination 'hole' seems to be the driving force for the preference of the acetate.

In the case of germanium, we have obtained mixtures of the acetate and chloride complexes and this result is probably due to the minor steric requirements of germanium versus tin.

However, it is possible to interconvert the counterion in both Ge or Sn complexes: by shaking a methanolic solution of [Me(OMC)OAc] with NaCl dissolved in diluted HCl we obtained [Me(OMC)Cl], identical to an authentic specimen, and, on the other hand, using $AgNO_3$ and NaOAc the product obtained was [Me(OMC)OAc].

When [Sn(OMC)OAc] was column chromatographed on basic alumina we obtained the corresponding hydroxo complex. In this case the axial reactivity of Sn corrolato seems to be similar to that of the corresponding porphyrinato complexes [7].

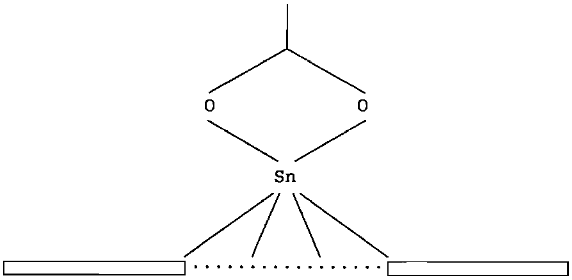

Fig. 1. Coordination type of Sn(OMC)OAc.

Indium corrolate has been obtained by cyclization of BD or by reaction of the preformed macrocycle with $InCl_3$ in DMF.

The yields of these syntheses are lower than those obtained with Sn or Ge and also the chromatographic purification is very difficult because of the lability of In corrolate.

When the synthesis is performed using BD as starting material variable amounts of metal free corrole have been obtained which seems to indicate that demetalation of the In complex occurs in these conditions.

The 400 MHz ^{1}H NMR spectrum of In corrolate shows two singlets at 10.32 (*meso*-H) and 3.70 (methyls) ppm, probably because of the casual superimposition of the different resonances due to the *meso*-protons as observed in the case of Sn and Ge acetate complexes.

Zn corrolate can be obtained by refluxing the preformed macrocycle with Zn acetate in pyridine solution. Other metal(II) corrolates have been described in the literature: the Ni(II) and Pd(II) derivatives have been reported to be paramagnetic and it has not been possible to characterize them via NMR. The location of the aminic proton not involved in binding the metal has not been resolved: the hypothesis has been reported that such a proton would be located at C-10 [9].

The Zn complex is not paramagnetic; on the basis of its 400 MHz ^{1}H NMR spectrum the complex can be formulated as {$[ZnOMC]^-[PyH]^+$}.

All the metallo-corrolates are aromatic, as shown by their electronic spectra, where an intense Soret-like band is present in the high-energy region. These spectra are very similar to those of the corresponding *etio*-type metallo-porphyrinates and they can be classified as normal spectra [10].

The lower symmetry of the corrole ring does not seem to influence the electronic spectra, but the lack of MO calculation does not allow a more detailed discussion.

The ability of the corrole ring to chelate main group metals seems to indicate that the possibility exists to build a Periodic Table for metallo-corrolates and confirms the versatility of this macrocycle.

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