Synthesis and Heterodimetallic Complexes of Lateral Macrobicyclic Cryptands

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The macrobicyclic molecules (**1a**—**c**) have been synthesized; they are heteroditopic ligands combining a 'soft' and a 'hard' binding subunit, which form lateral dinuclear cryptates such as [Rh^+–CO, $M^{n+} \subset$ (**1a**—**c**)] by selective complexation to a given site.

Lateral macrobicyclic cryptands are coreceptor molecules[1] based on the combination of two different binding subunits (heteroditopic), a chelating one and a macrocyclic one; they are therefore dissymmetrical in nature.[2a] When binding two metal cations they should form dinuclear cryptates with specific features: (i) whether homometallic or heterometallic, the two cations will differ in number of free co-ordination sites and redox properties; (ii) a soft, redox active site may be combined with a hard Lewis acid centre; (iii) whereas the cations may interact directly at short distances, at longer separations cascade type binding of substrate(s) between the two metal ions may induce activation, catalysis, and condensation of the bound species.[2]

Dinuclear macrocyclic and macropolycyclic ligands have been actively studied in recent years.[2,3] We describe here the synthesis and some properties of ligands belonging to the lateral macrobicyclic type,[2a] which combine a 'soft' pyridyldithio (PyS_2) chelating subunit with the 'hard' azoxamacrocycles [12]-N_2O_2, [15]-N_2O_3, and [18]-N_2O_4 in (**1a**—**c**) respectively. The synthetic strategy involved attachment of lateral chains to the macrocycles followed by cyclisation to give the macrobicyclic structures. We reported earlier a cryptand of the same class (**2**) whose dinuclear Cu^{II} complex displayed strikingly different electrochemical properties for the two cations, which had a difference in redox potential of *ca.* 0.5 V.[2a,4,5]

Reaction of the diazapolyoxamacrocycles (**3a**—**c**)[6] with 3-oxaglutaric anhydride in CH_2Cl_2 gave the diamido-diacids (**4a**—**c**), which were reduced with diborane in tetrahydrofuran (THF) (reflux, 2 h) to the diamino-diols (**5a**—**c**) (colourless oils; 80—90% overall yield). These were treated with neat $SOCl_2$ to give the dichlorides (**6a**—**c**) (colourless oils; 80—90% yield) which were kept as their dihydrochloride salts. Reaction of (**6a**—**c**) with the disodium salt of 2,6-

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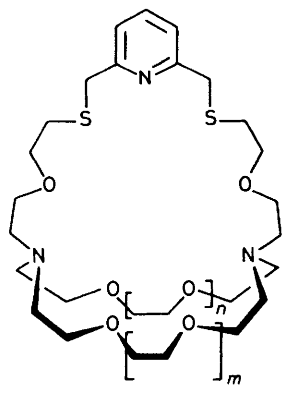
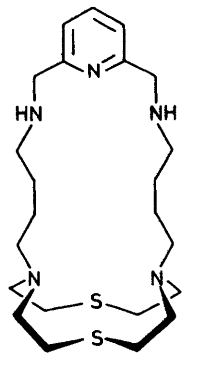
† UA 422 of the CNRS.

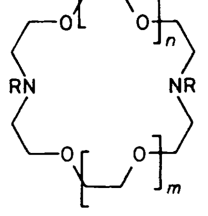


(1)

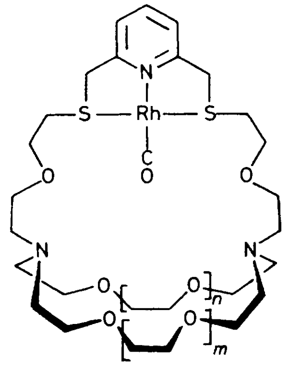
a ; $m = n = 0$
b ; $m = 1, n = 0$
c ; $m = n = 1$



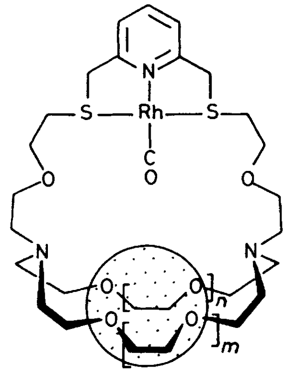
(2)



(3) R = H
(4) R = $COCH_2OCH_2CO_2H$
(5) R = $CH_2CH_2OCH_2CH_2OH$
(6) R = $CH_2CH_2OCH_2CH_2Cl$



(7a-c)



(8a-c)

dithiomethylpyridine in propan-2-ol (reflux, 6 h, concentration *ca.* 3—4 mM for each reagent) gave the desired macrobicyclic cryptands (**1a—c**) as colourless oils in *ca.* 55% yield.‡

Because of their heteroditopic nature, the cryptands (**1a—c**) may be expected to exhibit haptoselectivity,[1] *i.e.* preferential binding of a metal ion of given type and/or oxidation state to each subunit. Heterobinuclear Fe^{III}–Cu^{II} complexes of a macrobicycle containing a porphyrin macrocycle and a PyS_2 unit have been reported.[7]

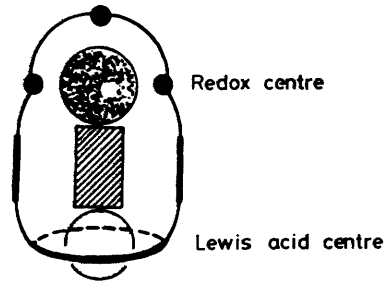


Figure 1. Principle of dimetallic activation of a substrate forming a cascade complex with a dinuclear cryptate of lateral macrobicyclic type combining a 'hard' (Lewis acid) and a 'soft' (redox) metallic site.

The complexation of Cu^{II} by (**1a—c**) was studied by following the changes in visible absorption spectra occurring on titration with copper trifluoromethanesulphonate in propylene carbonate. Using as references the spectra of the Cu^{II} complexes of (**3a—c**) ($\lambda_{max.}$ 710—790 nm, ε 50—90)[8—10] and of PyS_2 ligands[11] ($\lambda_{max.}$ 680 nm, ε 650),[9] the data indicated that Cu^{II} was bound first preferentially to the macrocyclic subunit and then to the PyS_2 groups, giving finally a complex with a stoicheiometry of 2 : 3 ligand : Cu^{II} (from a Job plot). Such a species was isolated and characterized in the case of $[(\mathbf{1a})_2(Cu^{2+})_3](BF_4)_6 \cdot 3H_2O$. These results are in accord with the formation of strong 1 : 1 Cu^{II} complexes by macrocycles (**3a—c**);[8,10] furthermore, since Cu^{II} gives a 1 : 1 complex with a macrocycle containing two PyS_2 units,[11a] one may propose that in the 2 : 3 complexes a Cu^{II} ion is bound to each macrocycle and the third cation is bound to two PyS_2 units, one from each macrobicycle.

When (**1a—c**) were allowed to react with $[Rh_2Cl_2(CO)_4]$ in methanol, the spectral properties of the solutions obtained indicated the formation of 1 : 1 complexes containing an $(Rh\text{–}CO)^+$ unit with a terminal carbonyl group [ν 2000—2010 cm^{-1}; δ (^{13}CO) 188.7, $J(Rh\text{–}^{13}CO)$ 69—70 Hz]; large downfield shifts (*ca.* 10 p.p.m.) were observed for the CH_2S ^{13}C n.m.r. signals on going from the free ligands to the complexes, whereas the other ^{13}C signals were little affected. These data agree with the formation of haptoselective complexes (**7a—c**) in which an $(Rh\text{–}CO)^+$ group is bound to the 'soft' PyS_2 subunit of (**1a—c**) in square planar coordination. Such species have been reported with other ligands containing the PyS_2 fragment.[11a] Complex (**7a**) was isolated as small reddish crystals of its monoprotonated hexafluorophosphate.‡

Since in (**7a—c**) the carbonyl group should be oriented towards the macrocyclic subunit, it was of interest to investigate the formation of hetero-dinuclear cryptates of type (**8a—c**).

Titration of the trifluoromethanesulphonates of (**7a—c**) (obtained from the chlorides with silver trifluoromethanesulphonate) with Cu^{II} trifluoromethanesulphonate in propylene carbonate gave an absorption band at 720—770 nm which increased on addition of up to 1 equiv. Cu^{II}, in agreement with binding of Cu^{II} to the macrocyclic units of (**7a—c**), thus giving dimetallic (Rh^{I}–CO, Cu^{II}) complexes of type (**8a—c**).

Several studies were carried out with anhydrous trifluoromethanesulphonate (TfO) or tetrafluoroborate salts of diamagnetic cations using ^{13}C n.m.r. spectroscopy and isotopically enriched ^{13}CO complexes (**7a—c**) in CD_3CN or $(CD_3)_2CO$. Addition of $LiPF_6$ or $Zn(TfO)_2$ to (**7a**), of AgTfO, $La(TfO)_3$, or $Al(TfO)_3$ to (**7b**), and of AgTfO, $Ba(BF_4)_2$, or $Cd(BF_4)_2$ to (**7c**) gave shifts of the CH_2 ^{13}C n.m.r. signals indicative of complexation of the cation to the 'hard' binding site, the macrocyclic unit. The dimetallic

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‡ All new compounds had spectral and microanalytical data in agreement with their structure.

complexes formed by reaction of (**7a**) with $LiPF_6$ and $Zn(BF_4)_2$ were isolated and characterized.‡ The n.m.r. parameters of the ^{13}CO groups were little affected by binding of the second cation, which led in all cases to small downfield shifts of *ca.* 1—2 p.p.m. and to a decrease in $J(Rh-^{13}CO)$ of 1 Hz or less. Also the vibrational frequency ν(CO) was unchanged.

The formation of haptoselective hetero-dimetallic cryptates of type (**8a—c**) depends on the relative size of the two partners; the cation may be found either on 'top' of the macrocycle (*e.g.* for [12]-N_2O_2) or inside the macrocyclic cavity (*e.g.* for the larger [15]-N_2O_3 and [16]-N_2O_4 rings).

In complexes (**8a—c**), orientation of the carbonyl group more or less towards the metal ion bound to the macrocyclic subunit may activate the CO substrate towards nucleophilic reactions at the carbon centre (see Figure 1). Reaction of co-ordinated CO with nucleophiles such as H_2O, H^-, HO^-, and MeO^-[12] may be enhanced by interaction of its oxygen with a Lewis acid[13] such as a metal ion,[13,14] bound for instance to a polyether chain in the ligand.[15] Lateral macrobicyclic cryptates represent a class of systems well suited (see Figure 1) for inducing processes of 'push–pull' dimetallic substrate activation.

Received, 17th April 1986; Com. 509

References

1 J. M. Lehn in 'Biomimetic Chemistry,' eds. Z. I. Yoshida and N. Ise, Kodansha, Tokyo, Elsevier, Amsterdam, 1983, p. 163.

2 (a) J. M. Lehn, *Pure Appl. Chem.*, 1980, **52**, 2441; (b) J. M. Lehn, in 'Frontiers of Chemistry (IUPAC),' ed. K. J. Laidler, Pergamon, New York, 1982, p. 265.

3 S. M. Nelson, *Pure Appl. Chem.*, 1980, **52**, 2461; *Inorg. Chim. Acta*, 1982, **62**, 39; D. E. Fenton, U. Casellato, P. A. Vigato, and M. Vidali, *ibid.*, 1982, **62**, 57; for heterotopic ligands, see also: A. D. Hamilton, J. M. Lehn, and J. L. Sessler, *J. Chem. Soc., Chem. Commun.*, 1984, 311; B. A. Boyce, A. Carroy, J. M. Lehn, and D. Parker, *ibid.*, 1984, 1546; D. Parker, *ibid.*, 1985, 1129.

4 J. Comarmond and J. M. Lehn, unpublished results; J. Comarmond, Thèse de Doctorat, Université Louis Pasteur, Strasbourg, 1981; for a cryptand closely related to (**2**), see: J. M. Lehn, C.-T. Wu, and P. Plumeré, *Acta Chim. Sinica*, 1983, 67.

5 J. P. Gisselbrecht and M. Gross, in Advances in Chemistry Series, No. 201, 'Electrochemical and Spectrochemical Studies of Biological Redox Components,' ed. K. M. Kadish, American Chemical Society, 1982, p. 109.

6 B. Dietrich, J. M. Lehn, J. P. Sauvage, and J. Blanzat, *Tetrahedron*, 1973, **29**, 1629.

7 M. J. Gunther, L. N. Mander, K. S. Murray, and P. E. Clark, *J. Am. Chem. Soc.*, 1981, **103**, 6784.

8 B. Spiess, F. Arnaud-Neu, and M. J. Schwing-Weill, *Helv. Chim. Acta*, 1979, **62**, 1531; E. Luboch, A. Cygnan, and J. F. Biernat, *Inorg. Chem.*, 1983, **68**, 201; F. Arnaud-Neu, M. Sanchez, R. Yahya, M. J. Schwing-Weill, and J. M. Lehn, *Helv. Chim. Acta*, 1985, **68**, 456.

9 A. Carroy, Thèse de Docteur-Ingénieur, Université Louis Pasteur, Strasbourg, 1984.

10 B. Spiess, Thèse de Doctorat-ès-Sciences, Université Louis Pasteur, Strasbourg, 1981.

11 (a) D. Parker, J. M. Lehn, and J. Rimmer, *J. Chem. Soc., Dalton Trans.*, 1985, 1517; (b) see also: G. Weber, *Inorg. Chim. Acta*, 1982, **58**, 27; E. Weber and F. Vögtle, *Chem. Ber.*, 1976, **109**, 1803.

12 C. P. Casey and S. M. Neumann, *J. Am. Chem. Soc.*, 1976, **98**, 5395; R. J. Trautman, D. C. Cross, and P. C. Ford, *ibid.*, 1985, **107**, 2355; D. C. Cross and P. C. Ford, *ibid.*, 1985, **107**, 585; K. R. Lane, R. E. Lee, L. Sallans, and R. R. Squires, *ibid.*, 1984, **106**, 5767; M. M. Harris, J. D. Atwood, M. E. Wright, and G. O. Nelson, *Inorg. Chem.*, 1982, **21**, 2117; W. Tam, M. Marsi, and J. A. Gladysz, *ibid.*, 1983, **22**, 1413; D. J. Darensbourg and A. Rokicki, *Organometallics*, 1982, **1**, 1865; M. A. Lilga and J. A. Ibers, *ibid.*, 1985, **3**, 590.

13 D. F. Shriver, Am. Chem. Soc. Symposium Series no. 152, 'Catalytic Activation of Carbon Monoxide,' ed. P. C. Ford, American Chemical Society, 1981, p. 1; see also, J. A. Labinger and J. S. Miller, *J. Am. Chem. Soc.*, 1982, **104**, 6856.

14 J. P. Collman, R. G. Finke, J. Cawse, and J. I. Brauman, *J. Am. Chem. Soc.*, 1978, **100**, 4766; F. Calderazzo and K. Noack, *Coord. Chem. Rev.*, 1966, **1**, 118; M. Mitay, W. Priester, and M. J. Rosenblum, *J. Am. Chem. Soc.*, 1978, **100**, 3620.

15 J. Powell, A. Kuksis, C. J. May, S. C. Nyberg, and S. J. Smith, *J. Am. Chem. Soc.*, 1981, **103**, 5941; J. Powell, M. Gregg, A. Kuksis, and P. Meindl, *ibid.*, 1983, **105**, 1064; J. Powell, S. C. Nyburg, and S. J. Smith, *Inorg. Chim. Acta*, 1983, **76**, L15.