A Dinuclear Rhodium–Carbonyl Cryptate of a Ditopic Macrocyclic Ligand

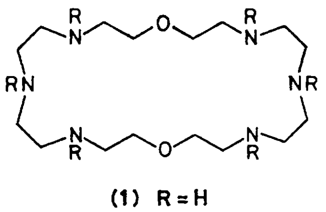
Jean-Pierre Lecomte,[a] Jean-Marie Lehn,*[a] David Parker,[a] Jean Guilhem,[b] and Claudine Pascard*[b]

[a] *Institut Le Bel, Université Louis Pasteur, 4 Rue Blaise Pascal, 67000 Strasbourg, France*

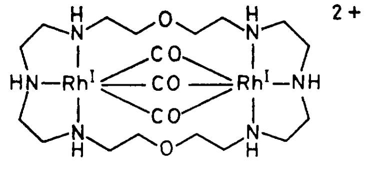
[b] *Laboratoire de Cristallochimie, Institut de Chimie des Substances Naturelles du CNRS, 91190 Gif-sur-Yvette, France*

Reaction of the ditopic hexa-aza-macrocycle (**1**) with tetracarbonyldichlorodirhodium(I) yields the dinuclear rhodium–carbonyl complex (**1**)–Rh_2, which may be considered as a cryptate of a triply bridged $[Rh(CO)_3Rh]^{2+}$ unit held inside the intramolecular cavity of the ligand.

Macropolycyclic structures containing several discrete subunits for metal ion binding should allow assembling of two or more cations into dinuclear or polynuclear cryptate complexes, which may further bind bridging ligands in a cascade fashion.[1,2]



(1) R = H



(1)–Rh$_2$

Such is the case in particular for ditopic macrocycles incorporating two chelating units. Thus, in recent years a number of dinuclear macrocyclic complexes of various transition metal cations have been obtained; a number of these contained bridging ligands and displayed novel structural and physicochemical properties (see refs. 1—5 and references therein).

We report here the synthesis, the structure, and some properties of a dinuclear rhodium(I)–carbonyl complex formed by the bis-diethylenetriamine macrocycle (**1**).[6–8] Macrocycle (**1**) has previously been shown to form dinuclear complexes with various first-row transition metal cations (Cu^{II}, Ni^{II}, Co^{II}) and to yield cascade complexes with bridging species (imidazolate, azido, hydroxo, peroxo anions).[7–10]

Reaction of an equimolar amount of tetracarbonyldichlorodirhodium(I), $(CO)_2Rh(Cl)_2Rh(CO)_2$ with macrocycle (**1**) in methanol gave a bright yellow solution (with rapid evolution of CO) from which a yellow microcrystalline solid was isolated in 88% yield by addition of an excess of ammonium hexafluorophosphate. Analytical and spectral data indicated that the product obtained was a dinuclear rhodium(I)–carbonyl complex (**1**)–Rh$_2$.

The i.r. spectrum of (**1**)–Rh$_2$ (Nujol) showed three sharp bands at 1800, 1810, and 1820 cm^{-1}; the complex prepared from 75% ^{13}C-enriched tetracarbonyldichlorodirhodium(I)† gave ν(CO) = 1760, 1769, and 1778 cm^{-1}.

The ^{1}H n.m.r. spectrum of (**1**)–Rh$_2$ at 298 K displayed two NH resonances in the ratio 1 : 2 at δ 5.35 and 4.31, which broadened as the temperature was lowered. A clearer view of this dynamic behaviour was given by the ^{13}C n.m.r. spectra of the ^{13}C-enriched complex. At 260 K, the carbonyl region showed two triplets in the ratio 1 : 2 at δ 214.5 and 211.9 p.p.m., each with J(Rh,C) 30 Hz. As the temperature was lowered, the upfield triplet broadened and split into two triplets, coalescence occurring at 210 K. At 170 K the spectrum contained three triplets in the ratio 1 : 1 : 1 centred at δ 214.4, 213.6, and 210.7 p.p.m. [J(Rh,C) 30 Hz]. At low temperature eight ^{13}C signals were observed for the CH$_2$N and CH$_2$O carbons of the macrocycle, whereas only four lines were present at 298 K at 66.5 (CH$_2$O), 53.4, 49.7, and 48.8 (CH$_2$N) p.p.m. The chemical shift and Rh–C coupling,[11] as well as the i.r.[12–14] data were consistent with the formulation of (**1**)–Rh$_2$ as a dinuclear rhodium complex containing bridging carbonyls, which undergo an intramolecular exchange process with a coalescence temperature of 210 K (k_c = 330 s^{-1}; $\Delta G_c^{\ddagger}$ = *ca.* 39 kJ mol^{-1}). The crystal structure of (**1**)–Rh$_2$ was determined and is shown in Figure 1.‡

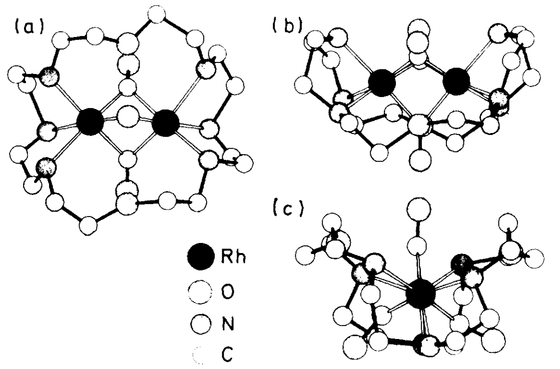


Figure 1. Crystal structure of the complex (**1**)–Rh$_2$; (a) view into the macrocyclic cavity, (b) side view, (c) view along the Rh–Rh axis.

Complex (**1**)–Rh$_2$ results from the *assembling* of two Rh^I ions and three CO groups by the ditopic macrocycle (**1**) into a triply bridged $[Rh(CO)_3Rh]^{2+}$ entity, bound to the two diethylenetriamine chelating subunits of the macrocycle and held inside the macrocyclic cavity in a cryptate fashion, $[Rh(CO)_3Rh \subset (\mathbf{1})]^{2+}$.

The co-ordination geometry of the two rhodium ions consists of two distorted octahedra sharing the face containing the three carbonyl carbons and having the three nitrogens of each diethylenetriamine subunit on the opposite faces. The average Rh–C and Rh–N distances are *ca.* 1.95 and 2.25 Å, respectively; the two oxygens are not co-ordinated and the Rh–CO–Rh angles are *ca.* 80°. The macrocycle is in a boat-like conformation forming a sort of a cup around the $[Rh(CO)_3Rh]^{2+}$ unit.

The very short Rh–Rh distance (2.58 Å) indicates the presence of a Rh–Rh bond, satisfying the 18e rule. It appears to be the shortest Rh–Rh single bond known.[16]§ Such a structure for the complex is isoelectronic with $Fe_2(CO)_9$ (Fe–Fe 2.52 Å) in which a similar $(CO)_3$ bridging unit has been found.[17] Although the encapsulation by the macrocycle may contribute to the shortening of the Rh–Rh distance, the

---

† Prepared by stirring a hexane solution of $Rh_2Cl_2(CO)_4$ under an excess of 90% ^{13}C-enriched carbon monoxide for 18 h.

‡ Crystals of complex [(**1**)–Rh$_2$·2PF$_6$, MeOH] were grown from acetone–methanol. *Crystal data:* An octahedric crystal of *ca.* 0.3 × 0.3 × 0.3 mm^3 was used for the structure determination. The cell parameters and intensity data were measured with a 4-circle graphite monochromated diffractometer, using Mo-K_α (λ 0.7107 Å) radiation. The crystals are orthorhombic, a = 14.218(7), b = 17.943(9), c = 13.054(6) Å. Lorentz and polarisation corrections were applied, but none was applied for absorption. The space group is $Pna2_1$, pseudo-$Pnam$, all heavy atoms (Rh and P) lying approximately at the same z-co-ordinate. There are 4 formula units in the cell; the linear absorption coefficient is 11 cm^{-1} and the calculated density is 1.90 g cm^{-3}. The structure was solved by the heavy atom method. From 5452 measured data, 2322 were used in the calculations [$I > 2.5\sigma(I)$]. A methanol molecule of crystallisation was located in the structure. Only the rhodium atoms were anisotropically refined. The weighting scheme was based on counting statistics. The final R-factor is 7.7%.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ Rh–Rh distances of 2.59, 2.63, and 2.66 Å are found in CO bridged dinuclear rhodium(I) complexes (ref. 15).

ligand is flexible enough to adjust to the geometrical requirements of the $[Rh(CO)_3Rh]^{2+}$ unit.

The temperature dependence of the ^{13}C n.m.r. spectrum may be attributed to a conformational process interconverting two equivalent dissymetric conformations in which all three CO groups are different but which retain a symmetry plane (σ_1) containing the three CO groups and the ligand oxygens, since three CO and eight ligand ^{13}C signals are observed at low temperature. When this process becomes fast it introduces an average symmetry plane (σ_2) containing the two rhodium atoms and the central nitrogens of each diethylenetriamine unit, thus giving two CO (ratio 2:1) and four ligand ^{13}C resonances. Because of the presence of the two heavy Rh atoms, the crystal structure is not accurate enough to ascertain the exact conformation involved. The structure shown in Figure 1 has no symmetry element at all, so that it should display sixteen ^{13}C signals for the ligand. It may well be that two conformational rate processes are present, one with a lower activation energy which introduces the average plane σ_1 and the second one, that observed here, yielding the effective plane σ_2. The first process might for instance involve restricted conformational motions in the ligand chains on each side of σ_1 and the second, a librational motion of the entire system about the Rh–Rh axis.

Preliminary experiments with the permethyl derivative (R = Me) of (**1**), indicate that, under similar conditions, this ligand also forms a dinuclear rhodium complex, containing, however, only terminally bound carbonyls with ν(CO) bands at 1959 and 1982 cm^{-1}.[12,13] This illustrates that simple alkyl substitution on the nitrogen sites of a polyamine macrocycle may introduce sufficient steric effects to hinder bridging by additional external ligands.

Complex (**1**)–Rh_2 is a dinuclear macrocyclic complex of *second row* transition metal ions. Few such complexes are known at present;[18] the bis-PtCl and bis-PdCl derivatives of (**1**)[2,19] and the bis-RhCO complex of a pyridine–sulphur containing macrocycle have also been obtained recently.[2,20]

The complexation properties displayed by macrocycle (**1**) illustrate how di- and poly-topic macrocycles and macropolycycles may assemble metal ions and bridging species inside an intramolecular cavity. The design of the macropolycyclic ligand (size, shape, nature and arrangement of the binding sites, *etc.*) provides control over the assembling process, thus in principle allowing the construction of *cluster cryptates*[1,2] of a desired structure.

D. P. thanks NATO for a post-doctoral fellowship.

Received, 26th November 1982; Com. 1274

References

1 J. M. Lehn, *Pure Appl. Chem.*, 1980, **52**, 2441.
2 J. M. Lehn, in 'IUPAC Frontiers of Chemistry,' ed. K. L. Laidler, Pergamon Press, Oxford, 1982, p. 265.
3 S. E. Groh, *Isr. J. Chem.*, 1976/77, **15**, 277.
4 U. Casellato, P. A. Vigato, D. E. Fenton, and M. Vidali, *Chem. Soc. Rev.*, 1979, **8**, 199.
5 S. M. Nelson, *Pure Appl. Chem.*, 1980, **52**, 2461.
6 J. M. Lehn, S. H. Pine, E. I. Watanabe, and A. K. Willard, *J. Am. Chem. Soc.*, 1977, **99**, 6766.
7 P. K. Coughlin, J. C. Dewan, S. J. Lippard, E. I. Watanabe, and J. M. Lehn, *J. Am. Chem. Soc.*, 1979, **101**, 265.
8 J. Comarmond, J. M. Lehn, P. Plumeré, Y. Agnus, R. Louis, R. Weiss, O. Kahn, and I. Morgenstern-Badarau, *J. Am. Chem. Soc.*, 1982, **104**, 6330.
9 P. K. Coughlin and S. J. Lippard, *J. Am. Chem. Soc.*, 1981, **103**, 3228.
10 R. J. Motekaitis, A. E. Martell, J. P. Lecomte, and J. M. Lehn, *Inorg. Chem.*, 1983, in the press.
11 B. E. Mann and B. R. Taylor, '^{13}C N.M.R. of Organometallics,' Academic Press, New York, 1981.
12 P. S. Braterman, 'Metal Carbonyl Spectra,' Academic Press, 1975; S. F. A. Kettle, *Top. Curr. Chem.*, 1977, **71**, 111.
13 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds,' Wiley–Interscience, New York, 3rd Edn., 1978.
14 J. P. Fair, M. M. Olmstead, C. H. Hunt, and A. L. Balch, *Inorg. Chem.*, 1981, **20**, 1182.
15 W. D. Jones, M. A. White, and R. G. Bergman, *J. Am. Chem. Soc.*, 1978, **100**, 6770; R. R. Burch, E. L. Muetterties, A. J. Schultz, E. G. Gebert, and J. M. Williams, *ibid.*, 1981, **103**, 5517.
16 F. A. Cotton, *Chem. Soc. Rev.*, 1975, **4**, 27.
17 F. A. Cotton and J. M. Troup, *J. Chem. Soc., Dalton Trans.*, 1974, 800.
18 G. C. Gordon, P. W. DeHaven, M. C. Weiss, and V. L. Goedken, *J. Am. Chem. Soc.*, 1978, **100**, 1003; M. Tsutin, R. L. Bobsein, R. Pettersen, and R. Haaker, *J. Coord. Chem.*, 1979, **8**, 245; K. M. Kadish, L. A. Bottomley, D. Schaefer, M. Tsutin, and R. L. Bobsein, *Inorg. Chim. Acta*, 1979, **36**, 219; A. E. Martin and J. E. Bulkowski, *J. Organomet. Chem.*, 1981, **217**, C29.
19 J. P. Lecomte and J. M. Lehn, unpublished results.
20 J. M. Lehn and D. Parker, unpublished results.