

- 5 E. N. Balko, *Studies Inorg. Chem.*, 1991, 11, 267
- 6 C. Comninellis and G. P. Verceri, *J. Appl. Electrochem.*, 1991, 21, 335
- 7 A. P. Bacon, Z. Twardowski and N. Tam, in "Modern Chlor-Alkali Technology", Volume 6, ed. R. W. Curry, R. Soc. Chem., 1995, p. 258
- 8 D. E. Grove, in "Modern Chlor-Alkali Technology", Volume 3, ed. K. Wall, Ellis Horwood, 1986
- 9 D. S. Cameron, R. L. Phillips and P. M. Willis, in "Modern Chlor-Alkali Technology", Volume 4, eds. N. M. Prout and J. S. Moorhouse, Elsevier Applied Science, 1986
- 10 Y. B. Vassiliev, E. P. Kovsman and G. N. Freidlin, *Electrochim. Acta*, 1982, 27, 937 and 953
- 11 D. S. Watkins, in "Fuel Cell Systems", eds. L. Blomen and M. Mugerwa, Plenum, New York, 1993, 493
- 12 K. B. Prater, *J. Power Sources*, 1996, 61, 105
- 13 S. Srinivasan, O. A. Velev, A. Parthasarathy, D. J. Manko and A. J. Appleby, *J. Power Sources*, 1991, 36, 299
- 14 M. P. Hogarth and G. A. Hards, *Platinum Metals Rev.*, 1996, 40, (4), 150
- 15 M. S. Wilson, J. A. Bett, T. A. Zawodzinski, J. A. Valerio and S. Gottesfeld, *Electrochem. Soc. Spring Meeting*, San Francisco, 1994, Abstract no. 626
- 16 A. S. Arico, Z. Poltarzewski, N. Giordano and V. Antonucci, *Electrochem. Soc. Spring Meeting*, Reno, 1995, Abstract no. 484
- 17 P. C. Foller and R. T. Bombard, *J. Appl. Electrochem.*, 1995, 25, 613
- 18 A. M. Couper and S. Bullen, *Inst. Chem. Eng. Symp. Series*, Rugby, 1992, 127, 49
- 19 P. C. Foller and G. H. Kelsall, *J. Appl. Electrochem.*, 1993, 23, 996
- 20 R. J. Allen, P. C. Foller, R. J. Vora, R. T. Bombard and M. Demarinis, *J.O.M.*, 1993, 45, (3), 49
- 21 P. C. Foller, R. J. Allen, R. T. Bombard and R. Vora, *Proceeding of the Fifth Int. Forum on Electrolysis in the Chemical Industry*, Fort Lauderdale, November, 1991, The Electrosynthesis Co. Inc., Lancaster, New York
- 22 J. D. Genders, E. F. Spiegel, D. Pletcher and N. L. Weinberg, *J. Appl. Electrochem.*, submitted
- 23 D. Pletcher and F. C. Walsh, in "Electrochemistry for a Cleaner Environment", eds. J. D. Genders and N. L. Weinberg, The Electrosynthesis Co. Inc., Lancaster, New York, 1992
- 24 Olin Corporation, *U.S. Patent* 5,294,319
- 25 L. Lipp and D. Pletcher, *Electrochim. Acta*, 1997, 42, 1101

A Rhodium Solvated Molecular Wire

One-dimensional inorganic compounds have been investigated for a number of years because of their interesting electrical properties and their predicted high temperature superconductivity; indeed the square-planar platinum cyano-complex ion, $[\text{Pt}(\text{CN})_4]^{2-}$, has been one of the commonest materials examined (1). Recently, there has been increased attention paid to molecular structures which can form molecular wires and act as connectors in molecular-scale electric devices (2). The controlling factors for the formation of these structures have been the ligands, which effectively govern the closeness between the metal atoms, and the electronic properties of the metals, which need incompletely filled bands to allow electron movement. However, there have been few infinite metal-metal bonded chains, because the ligands typically used in co-ordination compounds do not allow direct approach of the metal atoms along the axial direction.

Now, however, scientists from Michigan State University and Siemens in the U.S.A. and the Institut de Ciència de Materials de Barcelona in Spain, have succeeded in converting a discrete rhodium-rhodium bonded dimer into an infinite one-dimensional "polymer" array, $\{[\text{Rh}(\text{MeCN})_4](\text{BF}_4)_{1.5}\}_n$, by the one-electron reduction of $[\text{Rh}_2(\text{MeCN})_{10}](\text{BF}_4)_3$, in a cell also containing $[(\eta\text{C}_4\text{H}_9)_4\text{N}]\text{BF}_4$ in MeCN, with platinum electrodes and an applied current of 2 μA .

The unbridged rhodium compound was used in the investigation because it possessed only small, linear MeCN ligands, whose steric effects are minimal (3).

This rhodium polymer is the first, mixed valence, one-dimensional compound of rhodium, and is the only example of an infinite metal-metal bonded chain synthesised from a dinuclear precursor. The ligands are neutral donors, thus there is cationic charge on the chains which form the backbone. This contrasts with the partially oxidised tetracyanoplatinates which are anionic. The ligands may also be tailored, so it might be possible to produce insulating sheaths around the central chain of rhodium atoms, leading perhaps to liquid crystallinity, and allowing small changes in properties by varying the organic groups.

This novel rhodium chain polymer will enable the theory of one-dimensional materials to be tested, and using different ligands, will give insights into structures and transport properties.

References

- 1 A. E. Underhill, *Platinum Metals Rev.*, 1974, 18, (1), 21
- 2 V. Grosshenny, A. Harriman, M. Hissler and R. Ziessel, *Platinum Metals Rev.*, 1996, 40, (1), 26; *op. cit.*, 1996, 40, (2), 72
- 3 G. M. Finnis, E. Canadell, C. Campana and K. R. Dunbar, *Angew. Chem., Int. Ed. Eng.*, 1996, 35, (23/24), 2772