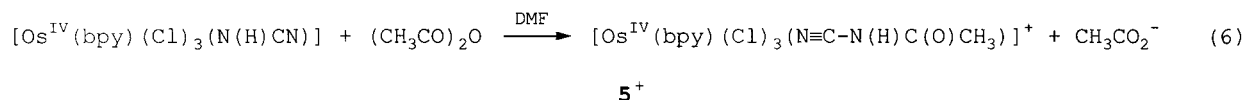
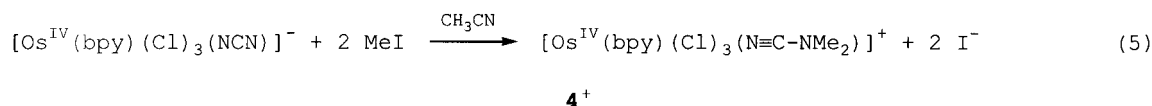
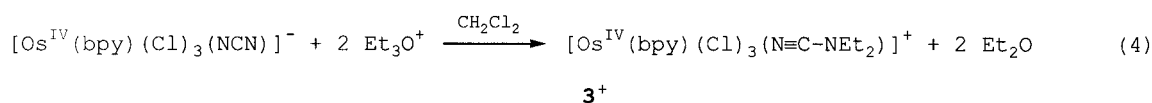
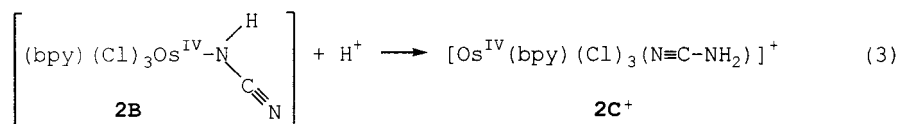


Direct evidence for monoprotonation at N_α comes from the IR spectra. In **2A**[−] and its ¹⁵N analogue, [Os^{IV}(bpy)(Cl)₃(¹⁵NCN)][−] (**2A**[−]), prepared from the ¹⁵N-nitrido complex precursor as in [Eq. (1b)], the IR band assigned as $\nu(\text{C}\equiv\text{N}_\beta)$ is at 1975 cm^{−1} for **2A**[−], and $\nu(\text{C}\equiv\text{N}_\beta)$ at 1977 cm^{−1} for **2A**[−]. Upon protonation, $\nu(^{14}\text{N}_\alpha\text{--H}) = 3230$, $\nu(\text{C}\equiv\text{N}_\beta) = 2187$ cm^{−1} for **2B** and $\nu(^{15}\text{N}_\alpha\text{--H}) = 3213$, $\nu(\text{C}\equiv\text{N}_\beta) = 2181$ cm^{−1} for **2B**⁺. Based on ¹H NMR spectra, **2A**[−] contains a paramagnetic d⁴ Os^{IV} center which results in a highly contact-shifted spectrum; **2B** is diamagnetic.

In the presence of a second equivalent of HPF₆ in CH₃CN, a second protonation occurs to give the Os^{IV}–cyanamido complex, [Os^{IV}(bpy)(Cl)₃(NCNH₂)]⁺ (**2C**⁺) [Eq. (3)], which



was isolated as the PF₆[−] salt. Diprotonation at N_β is supported by IR spectra which show $\nu(^{14}\text{N}_\alpha\equiv\text{C}) = 2280$ cm^{−1} for **2C**⁺ and $\nu(^{15}\text{N}_\alpha\equiv\text{C}) = 2249$ cm^{−1} for **2C**⁺; the bands for $\nu(^{14}\text{N}_\beta\text{--H})$ are 3332 ± 4 and 3200 ± 3 cm^{−1} for **2C**⁺ and **2C**⁺, respectively.

Dialkylation of **2A**[−] to give the corresponding Os^{IV}–dialkylcyanamido complexes, [Os^{IV}(bpy)(Cl)₃(NCNR₂)]⁺ (**3**⁺, R = Et, BF₄[−] salt and **4**⁺, R = Me, PF₆[−] salt), occurs under N₂ in reactions with triethyloxonium tetrafluoroborate ([Et₃O]⁺BF₄[−]) in CH₂Cl₂ and iodomethane (MeI) in CH₃CN, respectively [Eqs. (4) and (5)].

Acylation^[1d] of **2B** by acetic anhydride ((MeCO)₂O) in *N,N*-dimethylformamide (DMF) also occurs at N_β to give the Os^{IV}–acetylcyanamido complex, [Os^{IV}(bpy)(Cl)₃(NCN(H)C(O)Me)]⁺ (**5**⁺) [Eq. (6)], which was isolated as the PF₆[−] salt.

In all three cases, the differences in $\nu(\text{N}_\alpha\equiv\text{C})$ between the ¹⁴N_α and ¹⁵N_α forms are consistent with dialkyl or acyl addition at N_β , that is, **3**⁺: $\nu(^{14}\text{N}_\alpha\equiv\text{C}) = 2206$ and $\nu(^{15}\text{N}_\alpha\equiv\text{C}) = 2176$ cm^{−1}, **4**⁺: $\nu(^{14}\text{N}_\alpha\equiv\text{C}) = 2202$ and $\nu(^{15}\text{N}_\alpha\equiv\text{C}) = 2173$ cm^{−1}, and **5**⁺: $\nu(^{14}\text{N}_\alpha\equiv\text{C}) = 2208$ and $\nu(^{15}\text{N}_\alpha\equiv\text{C}) = 2179$ cm^{−1}.

There is also an extensive electron-transfer chemistry for the cyanoimido complexes reminiscent of the analogous hydrazido complexes. The electron transfer is based on electron occupation and deoccupation of levels largely localized in the Os–hydrazido π -bonding framework.^[4, 8] Cyclic voltammetry of the new compounds shows a series of reversible redox waves arising from the multiple oxidation/reduction of the osmium center (Table 1).

Our results provide a novel approach to the preparation of the NCN^{2−} ligand and its subsequent derivatization after

Table 1. Redox potentials for the new osmium compounds.^[a]

Compound	$E_{1/2}(\text{Os}^{\text{VI/V}})$	$E_{1/2}(\text{Os}^{\text{V/IV}})$	$E_{1/2}(\text{Os}^{\text{IV/III}})$	$E_{1/2}(\text{Os}^{\text{III/II}})$
1A	1.72	0.90	−0.40	−1.30
2A [−]	1.87	1.19	0.67	−0.90
3 ⁺			0.79	−0.63
4 ⁺			0.74	−0.58
5 ⁺			0.84	−0.55

[a] Potentials are given in Volts and measured against the sodium saturated calomel electrode (SSCE) in 0.1M TBAH/CH₃CN, (TBAH = tetrabutylammonium hexafluorophosphate). All processes are reversible.

coordination. The stepwise assembly of the dialkylated ligands provides a potentially general route to substituted cyanamido complexes that cannot be prepared directly because of polymerization of the preformed cyanamido organic precursors. Finally, the existence of multiple oxidation states and

the acid–base behavior of the NCN^{2−} ligand in the Os^{IV} complex may point to oxo-like reactivity based on proton-coupled electron transfer or atom transfer involving couples such as [Os^{VI}(bpy)(Cl)₃(NCN)]^{+/}[Os^V(bpy)(Cl)₃(N(H)CN)]^{+/} or [Os^{VI}(bpy)(Cl)₃(NCN)]^{+/}[Os^{IV}(bpy)(Cl)₃(NCNH₂)]^{+/}.

For full details on the preparation and characterization of all the new compounds see the Supporting Information.

Received: March 28, 2001 [Z16862]

- a) A. J. L. Pombeiro, *New J. Chem.* **1994**, 18, 163–174, and references therein; b) H. Fischer, C. Troll, *J. Organomet. Chem.* **1992**, 427, 77–90; c) W. Beck, H. Bock, R. Schlodde, *Z. Naturforsch. B: Chem. Sci.* **1974**, 29, 75–79; d) J. R. Balahura, R. B. Jordan, *J. Am. Chem. Soc.* **1971**, 93, 625.
- a) M. Becker, M. Jansen, *Z. Naturforsch. B: Chem. Sci.* **1999**, 54, 1375–1378; b) W. C. Wolsey, W. H. Huestis, T. W. Theyson, *J. Inorg. Nucl. Chem.* **1972**, 34, 2358; c) K. Zusai, T. Katayama, T. Ishida, T. Nogami, *Mol. Cryst. Liq. Cryst.* **2000**, 343, 439–444.
- a) A. J. L. Pombeiro, M. F. C. G. Silva, D. L. Hughes, R. L. Richard, *J. Organomet. Chem.* **1989**, 371, C45–C47; b) M. N. Ohnet, M. Jouan, G. Menard, A. Spasojevicde-Bire, N. Q. Dao, H. Fischer, D. Reindl, *Spectrochim. Acta Part A* **1996**, 52, 505–526, and references therein; c) F. Z. Hu, X. M. Zou, H. Z. Yang, L. H. Weng, *Chin. J. Chem.* **2000**, 18, 781–785.
- M. H. V. Huynh, E.-S. El-Samanody, K. D. Demadis, P. S. White, T. J. Meyer, *Inorg. Chem.* **2000**, 39, 3075–3085.
- D. W. Pipes, M. Bakir, S. E. Vitols, D. J. Hodgson, T. J. Meyer, *J. Am. Chem. Soc.* **1990**, 112, 5507–5514.
- a) P. Desjardins, G. P. A. Yap, R. J. Crutchley, *Inorg. Chem.* **1999**, 38, 5901–5905; b) L. M. D. R. S. Martins, J. J. R. F. daSilva, A. J. L. Pombeiro, R. A. Henderson, D. J. Evans, F. Benetollo, G. Bombieri, R. A. Michelin, *Inorg. Chim. Acta* **1999**, 291, 39–48; c) R. Reau, G. Bertrand,

Rev. Heteroat. Chem. **1996**, *14*, 137–163, and references therein; d) C. E. B. Evans, G. P. A. Yap, R. J. Crutchley, *Inorg. Chem.* **1998**, *37*, 6161–6167.

- [7] a) M. H. V. Huynh, P. S. White, T. J. Meyer, *Angew. Chem.* **2000**, *112*, 4267–4270; *Angew. Chem. Int. Ed.* **2000**, *39*, 4101–4104; b) M. H. V. Huynh, P. S. White, T. J. Meyer, *Inorg. Chem.* **2000**, *39*, 2825–2830.
 [8] M. H. V. Huynh, E.-S. El-Samanody, P. S. White, T. J. Meyer, *Inorg. Chem.* **1999**, *38*, 3760–3761.
 [9] M. H. V. Huynh, E.-S. El-Samanody, K. D. Demadis, P. S. White, T. J. Meyer, *J. Am. Chem. Soc.* **1999**, *121*, 1403–1404; b) M. H. V. Huynh, P. S. White, T. J. Meyer, *J. Am. Chem. Soc.* **1999**, *121*, 4530–4531.

Ferromagnetic Coupling through Spin Polarization in a Dinuclear Copper(II) Metallacyclophane**

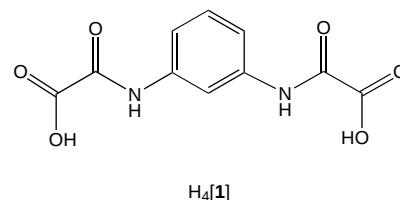
Isabel Fernández, Rafael Ruiz,* Juan Faus, Miguel Julve, Francesc Lloret,* Joan Cano, Xavier Ottenwaelder, Yves Journaux,* and M. Carmen Muñoz

In memory of Olivier Kahn

The design and synthesis of polynuclear coordination compounds with predictable magnetic properties have always interested inorganic chemists working in the field of magnetochemistry.^[1, 2] In particular, the preparation of ferromagnetically coupled dinuclear complexes appears intimately linked to the history of this relatively young discipline, namely molecular magnetism. Of the theoretical strategies to achieve a ferromagnetic spin alignment between two metal centers, those based either on orbital symmetry or spin polarization

effects are the easiest ones to be managed by the synthetic chemist.^[3] The second approach is particularly appealing and, however, has received more limited attention for metal complexes,^[4] when compared with the extensive work concerning high-spin organic molecules (polyradicals).^[5]

In our research into ligand design as a means to control the electronic and magnetic properties of polynuclear complexes,^[6, 7] we prepared the new ligand H₄[**1**], the parent acid



of *N,N'*-1,3-phenylenebis(oxamate). This ligand cannot act in a tetradentate manner towards a Cu^{II} center to give a monomeric four-coordinate copper(II) species, unlike the related ligand *N,N'*-1,2-phenylenebis(oxamate). Instead, it can self-assemble with Cu^{II} ions in a 2:2 ratio to give a dimeric copper(II) complex, [Cu₂(η²:η²-**1**)₂]⁴⁻, where the two ligands adopt the bisbidentate coordination mode, each donating one of its oxamate donor sets to each copper. In this case, two bis(oxamate)copper(II) spin-bearing residues are bridged by two *m*-phenylene moieties, which have already proven to be very effective ferromagnetic spin-coupling units in purely organic π-conjugated polyradicals.^[8] Here, we report the synthesis, crystal structure, and magnetic properties of the sodium salt of this novel oxamatocopper(II) complex of formula Na₄[Cu₂(**1**)₂] · 10H₂O (**2**).

The structure of **2** consists of noncentrosymmetric dinuclear copper(II) complex ions, [Cu₂(η²:η²-**1**)₂]⁴⁻, sodium cations, and both coordinated and noncoordinated water molecules (Figure 1). Actually, all twelve oxygen atoms from the four oxamate groups of the dicopper anion are bound to the sodium atoms, affording an intricate two-dimensional structure. The intramolecular copper–copper separation, Cu(1)⋯Cu(2), is 6.822(2) Å, while the shortest intermolecular ones, Cu(1)⋯Cu(1'') and Cu(2)⋯Cu(2'), are 6.335(3) and 6.999(3) Å, respectively.

The [Cu₂(η²:η²-**1**)₂]⁴⁻ unit is a metallamacrocycle composed of two bisbidentate oxamate ligands and two copper(II) cations. Moreover, owing to the almost parallel arrangement of the two benzene planes (dihedral angle of only 7.6(8)° and average interplanar separation of 3.4(1) Å), this dinuclear metallamacrocycle is of the cyclophane type (Figure 2a). In fact, a rather unusual near to perfect face-to-face π–π alignment of the two aromatic rings exists, such that a ring carbon atom lies just over the equivalent atom of the other ring (Figure 2b) with strong carbon–carbon contacts (C–C distances in the range 3.20(1)–3.57(2) Å). Hence, the resulting twelve-membered metallaza-linked [3.3]metacyclophane ring system (internal cavity of ca. 3.4 × 6.8 Å) has an approximate C_{2v} symmetry, with the copper basal planes being almost perpendicular to the benzene planes (dihedral angles in the range 72.1(3)–82.0(3)°). This imposes a non-

[*] Dr. R. Ruiz, Dr. I. Fernández
 Departament de Química Orgànica
 Facultat de Química, Universitat de València
 46100 Burjassot, València (Spain)
 Fax: (+34)963864328
 E-mail: rafael.ruiz@uv.es

Prof. F. Lloret, Prof. J. Faus, Prof. M. Julve
 Departament de Química Inorgànica
 Institut de Ciència Molecular
 Facultat de Química, Universitat de València
 46100 Burjassot, València (Spain)
 Fax: (+34)963864322
 E-mail: francesc.lloret@uv.es

Dr. Y. Journaux, Dr. J. Cano, X. Ottenwaelder
 Laboratoire de Chimie Inorganique, UMR 8613
 Université de Paris-Sud
 91405 Orsay (France)
 Fax: (+33)169154754
 E-mail: jour@icmo.u-psud.fr

Dr. M. C. Muñoz
 Departamento de Física Aplicada
 Universidad Politécnica de Valencia
 46071 Valencia (Spain)

[**] This work was supported by the Dirección General de Investigación Científica y Técnica (DGICYT) (Spain) (Projects PB97-1411 and PB97-1397) and the TMR Programme of the European Union (Contract No. ERBFM-RXCT980181). R.R. thanks the Ministerio de Educación y Ciencia (Spanish Government) for a grant.