Ion Pair Complexes from the Reduction of Metal(II)–Dibenzotetramethyltetra-aza[14]annulene Complexes

Stefano Ciurli,[a] **Edouard Marc Meyer,**[a] **Carlo Floriani,**[a]*† **Angiola Chiesi-Villa,**[b] **and Carlo Guastini**[b]

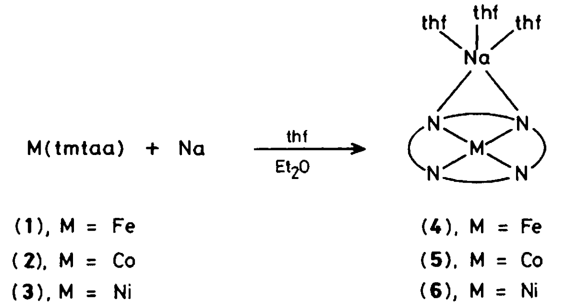
[a] *Chemistry Department, Columbia University, New York, N.Y. 10027, U.S.A.*
[b] *Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, 43100 Parma, Italy*

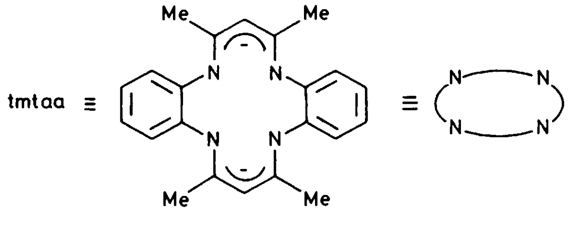
Ion pair complexes, $[M(tmtaa)Na(thf)_3]$ (M = Fe, Co, or Ni; tmtaa = dibenzotetramethyltetra-aza[14]annulene dianion; thf = tetrahydrofuran), in which both metal ions are associated with the macrocyclic ligand have been obtained from single-electron reduction of the parent metal(II) compounds with sodium metal; the crystal structure of one of the complexes is reported.

Reduction of macrocyclic metal complexes allows nucleophiles to be generated centred either at the ligand or at the metal.[1] Such nucleophiles play a significant role in electron transfer processes and in the functionalization of macrocyclic metal complexes, such as the introduction of an M–C functionality.[2] Their chemistry can be significantly affected by the form in which they occur: free anion or ion-pair form, and by the proximity of the two metal ions.[3,4] While many electrochemical studies are available on the redox properties

---

† *Present address:* I.C.M.A., Université de Lausanne, 3 Place du Chateau, CH-1005 Lausanne, Switzerland.





of a variety of macrocyclic complexes,[1] the isolation and structural characterization of reduced species is rare and limited to square-planar complexes containing *meso*-tetraphenylporphyrin[5,6] or tetradentate Schiff base derivatives[3] as ligands.

We report here the reduction of the metal(II)–7,16-dihydro-6,8,16,17-tetramethyldibenzo[b,i][1,4,8,11]tetra-azacyclotetradecinato, [M(tmtaa)] (M = Fe, Co, or Ni), complexes (**1**)—(**3**) having a saddle shape conformation,[7] and their isolation in the solid state as ion-pair complexes. Complexes (**1**)—(**3**) have been reduced in tetrahydrofuran (thf) with sodium sand in a 1 : 1 molar ratio. The resulting solution gave, upon addition of Et_2O, complexes (**4**)—(**6**), [M(tmtaa)-Na(thf)$_3$] as crystalline solids (yield *ca.* 60%).‡

Complexes (**4**)—(**6**) are very air-sensitive and reactive with a variety of substrates, their chemistry being under investigation. Complexes (**4**) and (**6**) are paramagnetic, μ = 2.92 and 1.89 μ_B at 292 K respectively, while the cobalt derivative (**5**) is diamagnetic. Electrochemical reductions carried out on complex (**3**)[8] and structural parameters we report here seem to suggest that the metal(I) designation is not a label of convenience only. The *X*-ray structures have been determined so far for complexes (**4**) and (**6**). We report here crystallographic details for complex (**4**)§ only, which crystallizes with a molecule of thf.

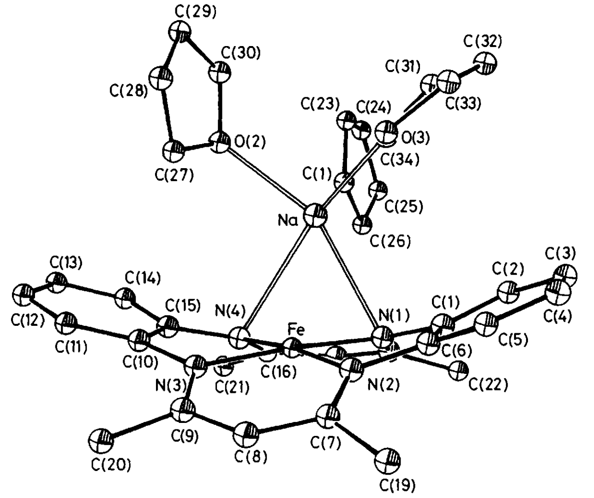


Figure 1. Complex (**4**), [Fe(tmtaa)Na(thf)$_3$]. Bond distances (Å): Fe–N(1), 1.895(8); Fe–N(2), 1.904(8); Fe–N(3), 1.926(8); Fe–N(4), 1.889(8); Fe ··· Na, 3.084(4); Na–N(1), 2.801(9); Na–N(4), 2.775(9); Na–O(1), 2.391(8); Na–O(2), 2.373(9); Na–O(3), 2.334(9). Fe is out of the N(1),N(2),N(3),N(4) plane by 0.0862(2) Å.

A perspective view of complex (**4**) is shown in Figure 1 with selected bond distances. Iron and sodium cations are both bonded to the macrocyclic ligand. The distance of the iron from the N_4 co-ordination plane and the M–N bond distances are significant structural parameters which may be related to variation of the metal ion radius, and so to the change in the oxidation state of the metal. The flattening of the co-ordination sphere in complex (**4**) with the iron out of the N_4 plane by 0.086(2) Å, the same distance being observed in the isoelectronic [Co(tmtaa)] (**7**),[9] is significant compared with the value of 0.114 Å reported for complex (**1**).[7] The increase in the oxidation state of the metal, along with other factors like the co-ordination number and the spin state, moves the metal from the N_4 plane by 0.600 Å in [Fe(tmtaa)Cl]·MeCN (**8**),[10] and 0.698 Å in [{Fe(tmtaa)}$_2$O]·MeCN (**9**).[11] The Fe–N bond distances (average value) are also affected by the same factors, varying from 2.054 Å [complex (**9**)], to 2.002 [complex (**8**)], 1.917(3) [complex (**1**)], and 1.903(9) Å [complex (**4**)]. The last value is close to that found for Co–N in the isoelectronic [Co(tmtaa)] (**7**).[9] An analogous trend has been observed for nickel, which is out of the N_4 plane in complex (**6**) by 0.006(4) Å, a similar value [0.075(2) Å] being found for copper in the isoelectronic [Cu(tmtaa)] (**10**).[9] Although the trends in the structural parameters mentioned above have been used[5,6] for the assignment of charge localization in tpp complexes (tpp = *meso*-tetraphenylporphyrin)], they can also be affected by additional factors. In fact these structural parameters seem to indicate that compounds (**4**)—(**6**) should be formulated as metal(I) complexes, though a definite conclusion cannot be reached at present. A noteworthy structural feature of complexes (**4**)—(**6**) is the association of the sodium cation with the macrocyclic structure. This ion pairing has already been observed in tpp–cobalt and –iron derivatives,[5,6] and in the reduced form of metal–Schiff base complexes.[3] The rather long Na–N distances [Na–N(1), 2.801(9); Na–N(4), 2.775(9) Å] are comparable with those found in [M(tpp)Na(thf)$_n$] complexes.[6] The resulting ion pair structure, which may even survive in non-co-ordinating solvents, is a sort of bifunctional complex,[4] which contains in a

---

‡ Satisfactory analytical data have been obtained.

§ *Crystal data:* $C_{38}H_{54}FeN_4NaO_4$, M = 709.7, monoclinic, space group $P2_1/c$, a = 9.152(2), b = 10.438(2), c = 39.607(10) Å, β = 93.89(3)°, U = 3775(2) Å^3, Z = 4, D_c = 1.249 g cm^{-3}, Mo-K_α radiation (λ = 0.7107 Å), μ(Mo-K_α) = 4.50 cm^{-1}; crystal dimensions: 0.16 × 0.25 × 0.40 mm. The structure was solved by the heavy atom method (Patterson and Fourier synthesis) and refined anisotropically by blocked full-matrix least-squares. For 2014 unique observed structure amplitudes [$I > 3\sigma(I)$] collected at room temperature on a Philips PW 1100 diffractometer in the range $6 < 2\theta < 47°$ the R value is 0.058. Most of the hydrogen atoms were located in a difference Fourier map and introduced as fixed contributors in the final stage of refinement. All calculations were carried out using SHELX 76. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

close proximity [Fe $\cdots$ Na, 3.084(4) Å] two different reactive sites. This significant characteristic of metal nucleophiles is important in view of the interaction with small molecules and organic functionalities.

We thank the U.S. Navy and Italian C.N.R. for financial support and the Fonds National Suisse de la Recherche Scientifique for a fellowship to E. M. M.

Received, 6th June 1986; Com. 772

References

1 J. Lewis and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1982, 1085; J. A. Switzer, J. F. Endicott, M. A. Khalifa, F. P. Rotzinger, and K. Kumar, *J. Am. Chem. Soc.*, 1983, **105**, 56; K. Kumar, F. P. Rotzinger, and J. F. Endicott, *ibid.*, 1983, **105**, 7064; M. Millar and R. H. Holm, *ibid.*, 1975, **97**, 6052; J. A. Streeky, D. G. Pillsbury, and D. H. Busch, *Inorg. Chem.*, 1980, **19**, 3148.

2 J. M. Pratt and P. G. Craig, *Adv. Organomet. Chem.*, 1973, **11**, 331.

3 G. Fachinetti, C. Floriani, P. F. Zanazzi, and A. R. Zanzari, *Inorg. Chem.*, 1979, **18**, 3469; S. Gambarotta, M. Mazzanti, C. Floriani, and M. Zehnder, *J. Chem. Soc., Chem. Commun.*, 1984, 1116; S. Gambarotta, F. Urso, C. Floriani, A. Chiesi-Villa, and C. Guastini, *Inorg. Chem.*, 1983, **22**, 3966.

4 S. Gambarotta, F. Arena, C. Floriani, and P. F. Zanazzi, *J. Am. Chem. Soc.*, 1982, **104**, 5082; S. Gambarotta, F. Arena, C. Floriani, and A. Gaetani-Mandredotti, *J. Chem. Soc., Chem. Commun.*, 1982, 835.

5 P. Doppelt, J. Fisher, and R. Weiss, *Inorg. Chem.*, 1984, **23**, 2958.

6 T. Mashiko, C. A. Reed, K. J. Haller, and W. R. Scheidt, *Inorg. Chem.*, 1984, **23**, 3192; C. A. Reed, *Adv. Chem. Ser.*, 1984, **201**, 333; S. Ciurli, S. Gambarotta, C. Floriani, A. Chiesi-Villa, and C. Guastini, *Angew. Chem.*, 1986, **25**, 553.

7 V. L. Goedken, S. M. Peng, J. Molin-Norris, and Y. Park, *J. Am. Chem. Soc.*, 1976, **98**, 8391.

8 J. C. Dabrowiak, D. P. Fisher, F. C. McElroy, and D. J. Macero, *Inorg. Chem.*, 1979, **19**, 2304; C. L. Bailey, R. D. Bereman, D. P. Rillema, and R. Nowak, *Inorg. Chem.*, 1984, **23**, 3956.

9 C. Floriani, A. Chiesi-Villa, and C. Guastini, unpublished results.

10 M. C. Weiss, B. Bursten, S. M. Peng, and V. L. Goedken, *J. Am. Chem. Soc.*, 1976, **98**, 8021.

11 M. C. Weiss and V. L. Goedken, *Inorg. Chem.*, 1979, **18**, 819.