DALTON
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Formation of a metallocyclophane *via* self-assembly of 2,3-bis(2,2′-bipyrid-6-yl)pyrazine and cobalt(II)

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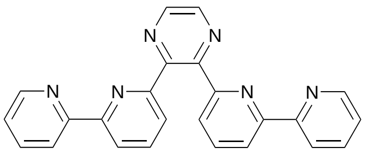
Electrospray mass spectrometric, proton NMR, UV-titrametric, electrochemical and X-ray crystallographic studies have shown that, in the presence of cobalt(II), 2,3-bis(2,2′-bipyrid-6-yl)pyrazine self-assembles to form a dimeric metallocyclophane which is also stable in solution.

The self-assembly of metallosupramolecular complexes from ligands having preorganized binding geometries and appropriate metallic centers is a topic of great current interest. The complexes thereby formed can exhibit various closed structures of rectangular geometry[1] as well as other forms.[2] Recently, we presented the synthesis of 2,3-bis(2,2′-bipyrid-6-yl)pyrazine L and related polyheterocycles[3] having two η^3-complexation sites connected through the pyrazine ring. Although L is, in fact, an isomer of 2,4-bis(2,2′-bipyridyl)pyrimidine and related compounds investigated by Lehn and co-workers,[4] we reasoned that the resonance interaction between the two pyrazine N atoms and the differing spatial arrangement of the appended 2,2′-bipyridyl groups in our ligand system would result in complexation behavior which differs greatly from those other compounds. Specifically, we were interested in the propensity of L to form closed, or cyclic oligomeric complexes. Our choice of the kinetically labile cobalt(II) ion to this end was based on the recent success of others in using it to assemble different supramolecular complexes.[5–8]

Accordingly, treatment of L with 1 equivalent of cobalt(II) diacetate in refluxing methanol resulted in a brick red solution. Isolation of the perchlorate salt and recrystallization from diisopropyl ether–acetonitrile gave brown needles of $[Co_2L_2][ClO_4]_4{\cdot}2H_2O$ **1**.† The results of combustion analysis and a UV-spectrophotometric titration of L with the same initial metal salt in methanol both indicated the limiting formation of a complex having a 1 : 1 ratio of metal to ligand. The electronic spectrum of **1** in acetonitrile displayed a charge-transfer band at 540 nm ($\varepsilon = 1250$ M^{-1} cm^{-1}), similar to some N_6-oligopyridine complexes of cobalt.[7] The low resolution electrospray mass spectrum exhibited major signals corresponding to $[Co_2L_2(ClO_4)]^{3+}$ ($m/z = 331.2$), $[CoL_2(ClO_4)]^+$ (934.4) and $[Co_2L_2(ClO_4)_3]^+$ (1192.8). The ^{1}H NMR spectrum in CD_3CN relative to $SiMe_4$ (Fig. 1) displayed 16 major resonances, all occurring in a range of *ca.* 120 ppm, which is consistent with both L occurring in a single, but non-symmetrical conformation in the complex, and *low-spin* Co^{II},[9] respectively.

Complex **1** is also electrochemically active. In acetonitrile solution containing $[NBu_4][ClO_4]$ as supporting electrolyte, the cyclic voltammogram of **1** exhibited a single oxidative wave at 0.248 V *versus* the ferrocene–ferrocenium couple. Other signals occurring at more negative potentials can be assigned with likelihood through literature comparison to either metal- or ligand-based reductions of the ligand skeleton.[10] The peak current of the oxidative signal was roughly twice that of the other reduction processes, which suggested that this signal arises from a metal-centered two-electron process. The absence of two such oxidation processes for **1** implied the lack of interactions between the metal centers.

These findings together suggest that L forms a cyclic, dimeric complex with cobalt(II) and perchlorate in solution. In order to determine the precise nature of the perchlorate salt **1**, its crystal structure was determined (Fig. 2).‡ The cobalt atom is bound on one side of ligand L in a terdentate fashion and on the opposite side solely from the pendant bipyridyl substituent, while the dihedral angle between these two binding domains of the same ligand molecule is 80°. The metal co-ordination sphere is completed by one acetonitrile molecule per cobalt. The central pyridyl pyrazine fragments are anti-parallel and slightly offset. Distances between the closest non-bonding pairs of atoms range from 3.12 [N(8)···N(17)] to 3.44 Å [C(12)···C(16)]. Both of these caveats resemble the arrangement found in some porphyrins and their zinc complexes in solution[13] and bespeak of electrostatic π-stacking interactions.[14] Although the non-bonding distances which characterise the cavity are within van der Waals distances, they are comparable to those of various



L

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† Indicated compounds gave satisfactory analyses for C, H and N [Found (calc. for **1**): C, 43.20 (43.40); H, 2.76 (2.73); N, 12.79 (12.65)% Found (calc. for **2**): C, 39.12 (39.10); H, 2.64 (2.19); N, 11.66 (11.40)%].

‡ Crystal data for $[Co_2L_2(MeCN)_2][ClO_4]_4{\cdot}3H_2O$: $C_{52}H_{44}Cl_4Co_2N_{14}O_{19}$, $M = 1428.67$, triclinic, space group $P\bar{1}$, $a = 11.054(2)$, $b = 11.910(2)$, $c = 12.080(2)$ Å, $\alpha = 73.46(3)$, $\beta = 68.51(3)$, $\gamma = 75.08(3)°$, $U = 1397.5(4)$ Å^3, $Z = 1$, $T = 100(2)$ K, final $R1$, $wR2$ and S are 0.0945, 0.2392 and 1.102 for 416 parameters, 5740 unique reflections, for which 4784 displayed $F_o > 4\sigma(F_o)$. A brown single crystal of **1** (0.70 × 0.18 × 0.49 mm) was mounted on an Enraf-Nonius CAD4 diffractometer sealed in a capillary under argon. Graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å) was used. Cell constants were obtained from a least-squares fit of the setting angles of 25 carefully centered reflections in the range $19 < 2\theta < 32°$. The data, collected at −173(1) °C using the ω–2θ scan technique, were corrected for Lorentz and polarization effects. No absorption correction was carried out. The structure was solved and refined by direct methods and Fourier-difference techniques performed on DEC Alpha workstations. The SHELXTL[11] software package was used for solution, refinement and artwork of the structures. Neutral-atom scattering factors were obtained from ref. 12. All non-hydrogen atoms were refined anisotropically. All H-atoms bound to carbon were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Residual positive and negative electron density (±3 e Å^{-3}) is found around the cobalt atom. Two waters of crystallization were found in the asymmetric unit, a third one is disordered near an inversion center [O(40)], and therefore given an occupancy factor of 0.5. Hydrogen bonds are formed between water molecules and the perchlorate anions, although the quality of the data prevented the localization of the hydrogen atoms. CCDC reference number 186/723.

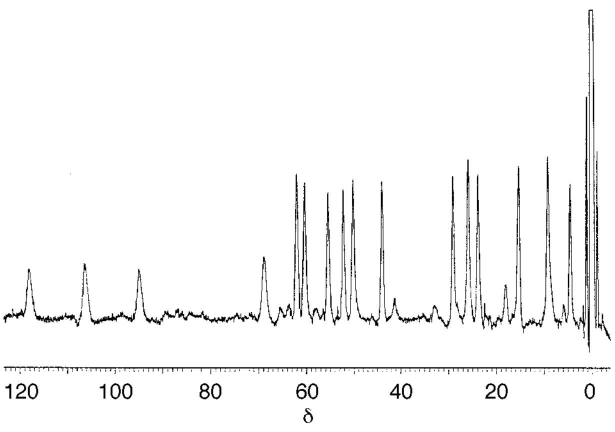

Fig. 1 Proton NMR spectrum of complex **1** (200 MHz, CD_3CN)

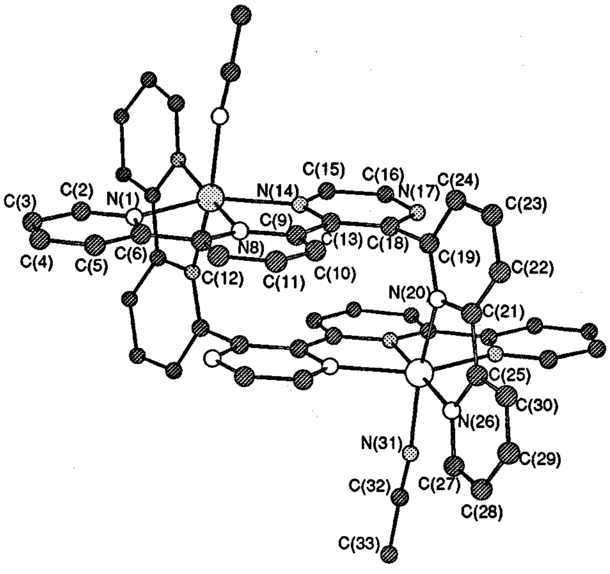

Fig. 2 Structure of complex **1** in the solid state. Hydrogen atoms, perchlorate counter ions and water molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Co–N(20) 2.202(4), Co–N(26) 2.089(4) , Co–N(40) 2.135(4), Co–N(14) 2.115(4), Co–N(8) 2.093(4), Co–N(1) 2.120(4); N(26)–Co–N(8) 175.2(2), N(26)–Co–N(14) 107.6(2), N(8)–Co–N(14) 75.0(2), N(26)–Co–N(1) 101.5(2), N(8)–Co–N(1) 76.3(2), N(14)–Co–N(1) 150.6(2), N(26)–Co–N(40) 91.1(2), N(8)–Co–N(40) 84.7(2), N(14)–Co–N(40) 90.8(2), N(1)–Co–N(40) 92.8(2), N(26)–Co–N(20) 77.2(2), N(8)–Co–N(20) 106.8(2), N(14)–Co–N(20) 93.9(2), N(1)–Co–N(20) 88.4(2), N(40)–Co–N(20) 168.3(2)

[*n*,*n*]cyclophanes.[15] The intermetallic distance is 6.44 Å. Metal–nitrogen bond parameters on the side of L binding terdentate are close to those of bis(2,2′:6′,2″-terpyridine)cobalt(II) perchlorate.[16]

The corresponding crystalline cobalt hexafluorophosphate complex $[Co_2L_2][PF_6]_4$ **2** was similarly prepared.† The results of its combustion analysis were in excellent agreement with a postulated composition of one metal atom for each molecule of L. However, the low resolution electrospray mass spectrum of **2** displayed a base signal corresponding to $[Co_3L_4(PF_6)_2]^{4+}$ ($m/z = 505.9$) and its ^1H NMR spectrum was characterized by 24 sharp signals at δ 0–82 and 5 broad ones at δ 100–203. The presence of signals in this latter range is indicative of *high-spin* Co^{II}.[9] The cyclic voltammogram of complex **2** in acetonitrile solution containing $[NBu_4][PF_6]$ exhibited reduction processes similar to those of **1**. Significantly, and in spite of repeated efforts, we could not observe any metal-centered oxidative processes; at most a weak and non-reproducible signal centered around *ca.* 0.34 V was seen. Thus, although many efforts to obtain crystals suitable for a crystal-structure determination of **2** were unsuccessful, we believe that the structure is also cyclic, albeit considerably more elaborate than that of **1**.

Summarizing, through judicious choice of counter ion, (oligopyridyl)pyrazine-based ligands can form discrete, cyclic, oligomeric complexes with Co^{II}. We are currently exploring the full extent of this phenomenon with L and other metal centers, as well as with more complicated ligand systems.

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