A pyridazine Schiff-base macrocycle hosts a dicobalt centre in five different redox states: evidence for a mixed valent Co^ICo^{II} species

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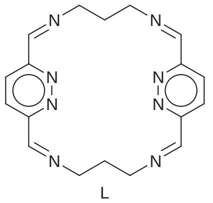
Electrochemical studies of $[Co^{II}_2L(MeCN)_4][ClO_4]_4$ 1, the first structurally characterised dicobalt complex to be bridged by pyridazine units, reveal two one-electron reductions as well as two one-electron oxidations at high potentials; one-electron reduction generates a mixed valent Co^ICo^{II} species which exhibits an intervalence charge transfer band at 965 nm.

Despite intense interest in cobalt(I) complexes as reactive centres for catalytic processes, such as CO_2 fixation and the reduction of water to dihydrogen or as models for vitamin B_{12}, there are relatively few examples of the isolation of such complexes in the absence of the stabilising effects of phosphines or phosphites.[1–4] Notable exceptions to this generalisation include structurally characterised complexes by Creutz *et al.*[3] and by Floriani and coworkers.[4]

We are studying complexes of chelating ligands based on 3,6-diformylpyridazine[5–8] and have found that the resulting dicopper(II) complexes exhibit positive reduction potentials (two well separated one-electron reductions),[7,8] and that dimanganese(II) complexes can be formed and are air stable.[6] These observations clearly indicate that our pyridazine-containing ligands are, as one might expect on the basis of their π-acceptor properties, good at stabilising low oxidation states of transition metal ions. Of these ligands, the macrocyclic ligands are expected to be particularly effective because strong chelation to the metal centres should hinder any subsequent decomposition reactions. Hence we have extended our studies to include a wide range of transition metal ions, with a view to stabilising and isolating unusually low oxidation state complexes.[6–8] Pyridazine- or phthalazine-bridged dicobalt(II) complexes are rare and, to our knowledge, no electrochemical studies have been reported for such complexes.[9] To date, there are no known examples with pyridazine-containing macrocyclic ligands. We report here on an air stable dicobalt(II) complex of the Schiff-base macrocyclic ligand L.



L

Transmetallation of the macrocyclic complex $[Pb_2L'][ClO_4]_4$ {L′ is the (4 + 4) analogue of L}[5,6] with cobalt(II) perchlorate in MeCN yields, after vapour diffusion of diethyl ether into the air stable solution, dark red crystals of $[Co_2L(MeCN)_4][ClO_4]_4$ **1**, in 57% yield.‡ The IR spectrum of **1** shows the presence of an imine absorption and the absence of absorptions due to either amine or carbonyl bonds. The FAB mass spectrum has a cluster of peaks consistent with the presence of $[Co_2L(ClO_4)_3]^+$, thus indicating that the original (4 + 4) Schiff-base macrocycle L′ had ring contracted to the (2 + 2) macrocycle L. This ring contraction, also observed in the case of the dicopper(II) and dimanganese(II) complexes,[6–8] was subsequently confirmed by single crystal X-ray structure analysis of a crystal obtained by slow evaporation of an acetonitrile solution of **1** to which an excess of sodium perchlorate had been added (Fig. 1).§

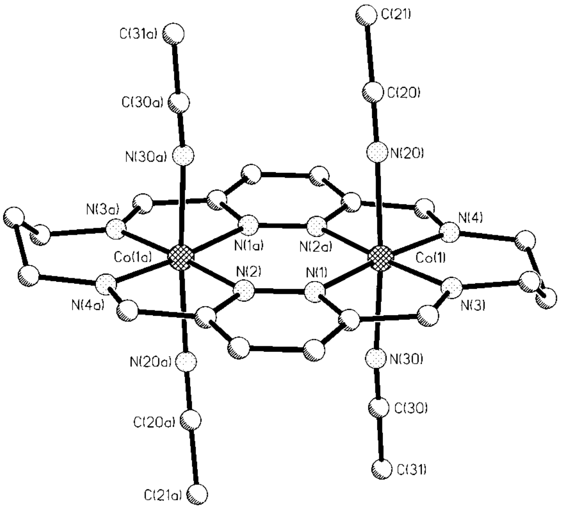


Fig. 1 Perspective view of one of the two independent cations of **1**, $[Co_2L(MeCN)_4]^{4+}$. Selected interatomic distances (Å) and angles (°): Co(1)–N(3) 1.984(4), Co(1)–N(4) 1.964(4), Co(1)–N(2a) 2.005(4), Co(1)–N(1) 2.013(4), Co(1)–N(30) 2.127(4), Co(1)–N(20) 2.135(4), Co(1)···Co(1a) 3.809(1); N(3)–Co(1)–N(4) 94.3(2), N(3)–Co(1)–N(2a) 175.5(2), N(4)–Co(1)–N(2a) 81.2(2), N(3)–Co(1)–N(1) 80.8(2), N(4)–Co(1)–N(1) 174.7(2), N(2a)–Co(1)–N(1) 103.7(2), N(3)–Co(1)–N(30) 92.8(2), N(4)–Co(1)–N(30) 88.8(2), N(2a)–Co(1)–N(30) 87.6(2), N(1)–Co(1)–N(30) 89.4(2), N(3)–Co(1)–N(20) 93.7(2), N(4)–Co(1)–N(20) 90.3(2), N(2a)–C0(1)–N(20) 85.9(2), N(1)–Co(1)–N(20) 92.1(2), N(30)–Co(1)–N(20) 173.5(2).

Cyclic voltammetry was carried out on $[Co_2L][ClO_4]_4$ in dry MeCN and revealed two one-electron reduction waves at remarkably high potentials ($E_{\frac{1}{2}} = -0.11$ V and $E_{\frac{1}{2}} = -0.33$ V, *vs.* Ag/0.01 M $AgNO_3$, Fig. 2) plus two one-electron oxidation waves at positive potentials ($E_{\frac{1}{2}} = +0.87$ V and $E_{\frac{1}{2}} = +1.06$ V, *vs* Ag/0.01 M $AgNO_3$, Fig. 2). The two reduction waves are tentatively assigned to $Co^{II}Co^{II} \rightarrow Co^{II}Co^I$ and $Co^{II}Co^I \rightarrow$

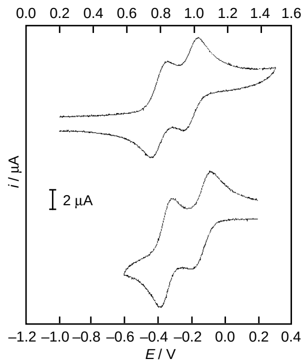


Fig. 2 Cyclic voltammogram of **1** in MeCN (1×10^{-3} M, 0.1 M NEt_4ClO_4, platinum counter electrode *vs.* Ag/0.01 M $AgNO_3$, 200 mV s^{-1}, in this system Fc–Fc$^+$ = +0.09 V).

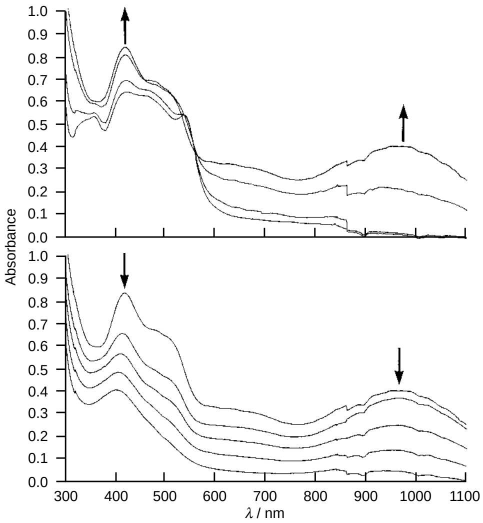


Fig. 3 Spectral changes during two step bulk electrolysis of **1** in MeCN. Top: first one-electron reduction ($E = -0.29$ V, 0.92 electron equivalents transferred). Bottom: second one-electron reduction ($E = -0.60$ V, 0.94 electron equivalents transferred).

Co^ICo^I reductions and the two oxidation waves to be $Co^{II}Co^{II} \rightarrow Co^{II}Co^{III}$ and $Co^{II}Co^{III} \rightarrow Co^{III}Co^{III}$ oxidations.¶

As no electrochemical studies have been reported on the handful of other known 1,2-diazine bridged cobalt complexes, it is not possible to make comparisons with these.[9] However, comparison with the redox properties of other related cobalt complexes, such as those provided by the systematic study of monocobalt complexes of a series of N_4-macrocycles by Busch and coworkers [$-2.21 < E_{\frac{1}{2}}(Co^{II} \rightarrow Co^I) < -0.72$ V *vs.* Ag/Ag$^+$ (0.1 M) in MeCN],[10] confirms that the reductions of **1** are, indeed, occurring at relatively high potentials. In that study the presence of an N_3 pyridine diimine or of two N_2 conjugated diimine groups in the N_4-macrocycle was found to greatly stabilise Co^I [$E_{\frac{1}{2}}(Co^{II} \rightarrow Co^I) = -0.72$ V and -0.86 V *vs.* Ag/Ag$^+$ (0.1 M) in MeCN, respectively].[10] Similarly, as the pyridazine macrocycle L incorporates imine bonds conjugated with pyridazine units an even greater enhancement of stability of Co^I results. In fact the observed potentials for **1** fall close to the range normally observed for oxidation of Co^{II} to Co^{III}.[11] For example, in the Busch complexes mentioned earlier the potentials for this oxidation process fall in the range -0.09 to $+0.17$ V *vs.* Ag/Ag$^+$ (0.1 M).[10] Again this is in clear contrast with the substantially more positive potentials observed for the oxidation processes of **1**, which presumably result from the build up of positive charge on the complex (+6 on the fully oxidised complex).

It is important to note that in our dicobalt(II) complex the two reductions and the two oxidations all occur in separate one electron steps: in the case of the reductions they are separated by 220 mV ($K_c = 5.24 \times 10^3$) whereas the oxidations are separated by 190 mV ($K_c = 1.63 \times 10^3$). Hence the mixed valent redox products are moderately stable. Preliminary spectroelectrochemical studies of the reduction processes indicate the existence of an intervalence charge transfer band in the mixed valent Co^ICo^{II} complex, with the growth of a broad band centred at 965 nm (2790 dm^3 mol^{-1} cm^{-1}) as the first electron is added to **1**, followed by bleaching of this band as the second electron is added (Fig. 3).‖ Further work, including solvent and temperature dependence studies, is necessary to confirm this. In contrast, oxidation of **1** does not result in a long wavelength absorption so in this case the mixed valent state appears to be valence localised.

The redox chemistry of the complexes derived from the macrocyclic ligand L is clearly rich: the ability of this ligand to stabilise dinuclear complexes in low oxidation states is very exciting and the reactivity of these complexes is being explored. Further characterisation of all of the redox states by, as appropriate, EPR or NMR spectroscopy, is underway, along with attempts to isolate each species. Finally, these ligands allow us to systematically study the magnetic exchange properties of unique pyridazine-bridged complexes and this feature of **1** is also under investigation.[8]

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Notes and References

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‡ Satisfactory C, H, N, analysis was obtained for acetonitrile-free **1** (the coordinated acetonitrile molecules are lost on drying *in vacuo*).

§ *Crystal data* for **1**: $C_{26}H_{32}Cl_4N_{12}O_{16}$, dark red block, 0.80 × 0.46 × 0.10 mm, triclinic, space group $P\bar{1}$, $a = 10.993(2)$, $b = 11.768(2)$, $c = 17.008(3)$ Å, $\alpha = 86.952(10)$, $\beta = 87.634(11)$, $\gamma = 64.321(14)°$, $U = 1979.6(5)$ Å^3, $Z = 2$, $\mu = 1.19$ mm^{-1}. Data were collected at 170 K on a Siemens P4 four-circle diffractometer using graphite-monochromated Mo-Kα radiation. 8997 Reflections were collected in the range $4 < 2\theta < 54°$ and the 8495 independent reflections were used in the structural analysis after a semi-empirical absorption correction had been applied. The structure was solved by direct methods (SHELXS-86)[12] and refined against all F^2 data (SHELXL-93)[13] to $R1 = 0.0596$ [for 5483 $F > 4\sigma(F)$; $wR2 = 0.53$ and goodness of fit = 1.04 for all 8495 F^2; 554 parameters; all non-hydrogen atoms anisotropic]. CCDC 182/833.

¶ The analogous dizinc complex shows no redox activity in the range -0.4 to $+1.5$ V, *vs.* Ag/0.01 M $AgNO_3$, under the same conditions.

‖ The cyclic voltammogram is unchanged after the two-electron reduction of **1** is complete.

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