

A dicobalt(II) complex of a triazolate-containing macrocycle reacts with nitromethane to yield an organometallic dicobalt(III) complex

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The synthesis and structures of a dicobalt(II) complex and an unusual organometallic dicobalt(III) complex of the triazolate-containing Schiff-base macrocyclic ligand L^{2-} are presented.

Cobalt complexes of N^1, N^2 -bridging triazole or triazolate ligands have been recently reviewed.¹ This year we have reported the first examples of structurally characterised complexes of triazole-containing macrocycles, specifically some dicopper(II) complexes of the Schiff-base macrocyclic ligand L^{2-} , derived from the [2 + 2] condensation of 3,5-diacetyl-1*H*-1,2,4-triazole and 1,3-diaminopropane,² and dicobalt(II) complexes of the macrocyclic ligand $(L')^{2-}$, derived from the [2 + 2] condensation of 3,5-diacetyl-1*H*-1,2,4-triazole and 1,4-diaminobutane (Fig. 1).³ Incorporating the triazole or triazolate moiety into Schiff-base macrocycles in this way is a significant step forward in the development of new classes of triazole-based ligands.^{1,4} Such ligands are of considerable current interest because the resulting metal complexes are expected to exhibit properties of interest in, for example, efforts to develop new magnetic materials^{1,4,5} or photochemically driven molecular devices.⁶

In this paper we present the synthesis and characterisation of two dicobalt complexes of the ligand L^{2-} , $[Co^{II}_2LCl_2]$ (**1**) and $[Co^{III}_2LCl_2(CH_2NO_2)_2]$ (**2**),[†] the latter of which is especially intriguing. The organometallic complex **2** is readily, and was initially serendipitously, formed upon reaction of **1** with the nitromethane recrystallisation solvent in air.

The dicobalt(II) complex $[Co^{II}_2LCl_2]$ (**1**) is prepared by transmetalation of $[Pb^{II}_2L](ClO_4)_2$ (ref. 2) with a stoichiometric amount of $CoCl_2 \cdot 6H_2O$ in acetonitrile and subsequent reaction with two equivalents of NEt_4Cl . The addition of $CoCl_2$ leads to $PbCl_2$ precipitating out of the reaction mixture. The further addition of chloride anions provides axial ligands for the complexed cobalt centres. After centrifuging to remove the $PbCl_2$, the dark red solution was concentrated and diffused with diethyl ether, yielding dark red–violet single crystals suitable for X-ray diffraction. The infrared spectrum shows that the macrocycle is still intact. Detailed magnetic susceptibility measurements have yet to be undertaken on **1**, but from the study completed on the very similar compound $[Co^{II}_2L'Cl_2]$ (ref 3) it is expected that **1** contains two weakly antiferromagnetically coupled high-spin Co^{II} ions. The structure determination (Fig. 2) shows that the cobalt centres are five coordinate. The metal–metal distance is 4.2802(15) Å. The macrocycle is significantly bent with the triazolate ring mean planes intersecting almost at right angles [85.52(8)°]. The N_4 mean planes

of the two coordinating sites intersect at an angle of 35.56(5)°. The metal centres are raised above that plane towards the chloride ligands by 0.8355(12) Å. The $Co-N_{\text{triazolate}}$ bond lengths are significantly shorter than the $Co-N_{\text{imine}}$ bond lengths ($Co-N_{\text{triazolate}}$ average 2.07 Å, $Co-N_{\text{imine}}$ average 2.13 Å) as was observed in the related complex $[Co^{II}_2L'Cl_2]$ ($Co-N_{\text{triazolate}}$ average 2.06 Å, $Co-N_{\text{imine}}$ average 2.17 Å).³ The $Co-Cl$ bond distance is 2.2717(9) Å, almost the same as in $[Co^{II}_2L'Cl_2]$ (average 2.29 Å).³ The bond lengths for the first coordination sphere are consistent with the description of the cobalt centres in **1** as high-spin Co^{II} .

In an attempt to recrystallise **1** from nitromethane in air, some red crystals of **2** grew slowly and spontaneously. The structure determination reveals that in **2** the two cobalt centres are now octahedrally coordinated and are separated by 3.8088(16) Å (Fig. 3). The $Co-N_{\text{triazolate}}$ bond lengths are again shorter (average 1.83 Å) than the $Co-N_{\text{imine}}$ distances (average 1.93 Å), and overall both sets of bond lengths are significantly shorter than were observed for **1**. This is expected as the Co^{II} centres in **1** have been oxidised to, smaller, Co^{III} centres in **2**. The two cobalt(III) centres are small enough to fit into the coordination sites of the macrocycle without folding it and this leads to a 0.47 Å shorter metal–metal distance than was the case in **1**. The whole macrocycle is very flat with only the middle carbon atom of each of the two propylene lateral groups being significantly out of the macrocycle mean plane. The $Co-Cl$ distance, 2.3263(12) Å, is longer than in **1**, presumably because of the change to an octahedral geometry and the presence of a *trans* $Co-C$ bond.⁷ The $Co-C$ distance of 2.038(3) Å is slightly longer than those reported in the literature for a $Co^{III}-CH_2NO_2$ bond

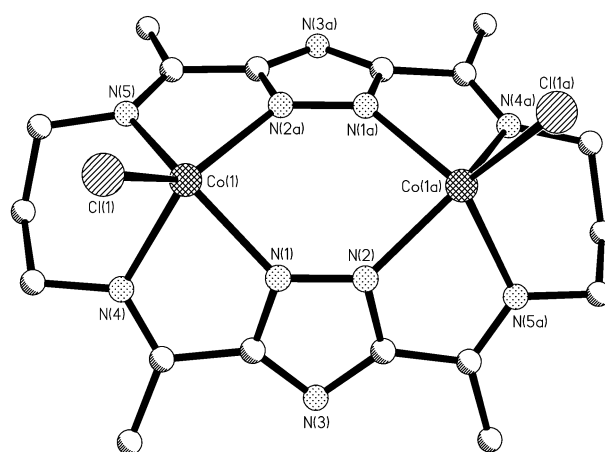


Fig. 2 Perspective view of complex **1**, $[Co^{II}_2LCl_2]$. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): $Co(1)-N(1)$ 2.062(2), $Co(1)-N(2a)$ 2.068(2), $Co(1)-N(5)$ 2.120(2), $Co(1)-N(4)$ 2.131(2), $Co(1)-Cl(1)$ 2.2717(9), $N(1)-Co(1)-N(2a)$ 85.22(8), $N(1)-Co(1)-N(5)$ 134.25(9), $N(2a)-Co(1)-N(5)$ 76.65(8), $N(1)-Co(1)-N(4)$ 76.41(8), $N(2a)-Co(1)-N(4)$ 131.71(8), $N(5)-Co(1)-N(4)$ 85.02(9), $N(1)-Co(1)-Cl(1)$ 110.38(6), $N(2a)-Co(1)-Cl(1)$ 132.80(6), $N(5)-Co(1)-Cl(1)$ 122.77(7), $N(4)-Co(1)-Cl(1)$ 95.49(7), $N(2)-N(1)-Co(1)$ 134.37(15). Symmetry transformation used to generate equivalent atoms: $-x, y, -z + 3/2$.

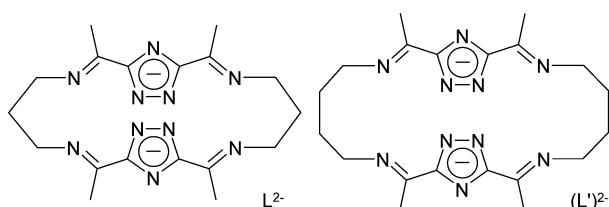


Fig. 1 The ligands L^{2-} and $(L')^{2-}$.

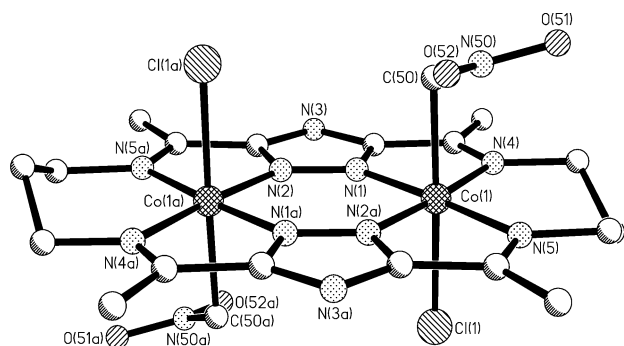


Fig. 3 Perspective view of complex **2**, $[\text{Co}^{\text{III}}_2\text{LCl}_2(\text{CH}_2\text{NO}_2)_2]$. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): Co(1)–N(2a) 1.829(3), Co(1)–N(1) 1.840(3), Co(1)–N(4) 1.931(3), Co(1)–N(5) 1.936(3), Co(1)–C(50) 2.038(3), Co(1)–Cl(1) 2.3263(12), C(50)–N(50) 1.453(5), N(50)–O(52) 1.243(4), N(50)–O(51) 1.245(4), N(2a)–Co(1)–N(1) 94.99(12), N(2a)–Co(1)–N(4) 174.88(12), N(1)–Co(1)–N(4) 79.91(13), N(2a)–Co(1)–N(5) 79.94(13), N(1)–Co(1)–N(5) 174.94(13), N(4)–Co(1)–N(5) 105.15(13), N(2a)–Co(1)–C(50) 89.59(13), N(1)–Co(1)–C(50) 86.89(13), N(4)–Co(1)–C(50) 89.55(13), N(5)–Co(1)–C(50) 93.16(13), N(2a)–Co(1)–Cl(1) 90.96(10), N(1)–Co(1)–Cl(1) 90.52(10), N(4)–Co(1)–Cl(1) 89.68(10), N(5)–Co(1)–Cl(1) 89.45(9), C(50)–Co(1)–Cl(1) 177.39(10), N(2)–N(1)–Co(1) 133.0(2), N(1)–N(2)–Co(1a) 132.0(2), N(50)–C(50)–Co(1) 111.8(2), O(52)–N(50)–O(51) 121.6(4), O(52)–N(50)–C(50) 122.1(4), O(51)–N(50)–C(50) 116.3(4). Symmetry transformation used to generate equivalent atoms: $-x, -y + 2, -z$.

(range: 1.99–2.00 Å).⁸ In fact, prior to this work, only three complexes with a nitromethyl anion coordinated to a cobalt centre, and thus forming a cobalt–carbon bond, have been structurally characterised.⁸ All of the three are mononuclear Co^{III} complexes containing two acyclic dimethylglyoximate ligands. The remaining axial position is occupied by either a pyridine, 1,2-dimethylimidazole or 1,5,6-trimethylbenzimidazole donor, forming an overall octahedral coordination sphere around the cobalt(III) centre.

The magnetic moment of **2**, at room temperature, has been determined and the complex was found to be diamagnetic, in agreement with the presence of two low-spin Co^{III} centres. Unfortunately, the complex is, without decomposition, insoluble in all common solvents which prevented further characterisation. However, a key finding is that the infrared spectrum of **2**, in addition to showing that the macrocycle is intact, shows a clear NO stretch at 1557 cm^{-1} ,⁹ which is absent in the spectrum of **1**.

Crystals of **2** were also grown accidentally when trying to crystallise **1** by diethyl ether vapour diffusion into an acetonitrile reaction solution, but using diethyl ether which was contaminated with nitromethane from a previous diffusion experiment. This shows the very strong tendency of this dicobalt complex to react, in air, with nitromethane.

In forming **2** clearly Co^{II} has been oxidised to Co^{III} and some of the nitromethane solvent has, in the absence of added base, lost a methyl proton and coordinated to the cobalt centre forming a Co–C bond. It is surprising that in **2** the two chloride ligands are *trans* to each other whilst in **1** they are *cis*. This may be an indication that the mechanism proceeds *via* other intermediates rather than directly from **1**. Investigation of the formation, properties and reactivity of such Co–C bonds is of interest for comparison with vitamin B_{12} structural and functional models and to aid in understanding the functioning of vitamin B_{12} itself.⁷ Therefore the mechanism of formation of **2** and further reactivity studies are subject to ongoing research in this group.

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Notes and references

† All reagents and solvents were used as received. Acetonitrile was dried over calcium hydride and distilled prior to use. CAUTION! Whilst no problems were encountered in the course of this work, perchlorate mixtures are potentially explosive and should therefore be handled with appropriate care. $[\text{Pb}^{\text{II}}\text{L}](\text{ClO}_4)_2$ was prepared as reported previously by us.²

Preparation of $[\text{Co}^{\text{II}}_2\text{LCl}_2]$ (**1**) and $[\text{Co}^{\text{III}}_2\text{LCl}_2(\text{CH}_2\text{NO}_2)_2]$ (**2**): 100 mg (0.1 mmol) $[\text{Pb}^{\text{II}}\text{L}](\text{ClO}_4)_2$ was dissolved in 20 mL boiling acetonitrile. To the refluxing solution was added dropwise a solution of 47 mg (0.2 mmol) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 5 mL acetonitrile. After refluxing for 4 hours the precipitated PbCl_2 was separated by centrifugation. To the clear, brownish-red solution a solution of 36 mg (0.2 mmol) $\text{NEt}_4\text{Cl} \cdot \text{H}_2\text{O}$ in 5 mL acetonitrile was added dropwise and the solution refluxed for 3 hours prior to stirring overnight at room temperature. The mixture was centrifuged again to remove any insoluble material. One half of the clear solution was concentrated to *ca.* 5 mL, and red–violet single crystals of **1** were obtained by diethyl ether diffusion into this acetonitrile solution. The other half was evaporated to dryness (CAUTION!) and redissolved in a few mLs of nitromethane which was added dropwise. Red single crystals (of variable quality) grew out of the mixture within hours. Yield 14 mg (41%). Found: C, 34.34; H, 4.24; N, 23.95. $\text{C}_{20}\text{H}_{28}\text{N}_{12}\text{Co}_2\text{Cl}_2\text{O}_4$ requires C, 34.85; H, 4.09; N, 24.38%. IR (KBr disk) $\nu_{\text{max}}/\text{cm}^{-1}$: 2933, 1616, 1557, 1489, 1417, 1373, 1217, 749, 654. $\mu_{\text{eff}} = 0.1\ \mu_{\text{B}}$ (298 K).

Crystal data for **1** (red–violet blocks, 168(2) K): $\text{C}_{18}\text{H}_{24}\text{N}_{10}\text{Co}_2\text{Cl}_2$, $M = 569.23$, monoclinic space group $\text{C}2/c$, $a = 13.511(5)$, $b = 14.947(5)$, $c = 13.093(5)$ Å, $\beta = 119.745(4)^\circ$, $U = 2295.7(14)$ Å³, $Z = 4$, $\mu = 1.706\text{ mm}^{-1}$, 14740 reflections collected, $R_1 = 0.0333$ for 2089 $F > 4\sigma(F)$, $wR_2 = 0.0846$ and $\text{Goof} = 1.090$ for all 2352 data, 156 parameters, all non-hydrogen atoms anisotropic.

Crystal data for **2** (red, 168(2) K): $\text{C}_{40}\text{H}_{56}\text{N}_{24}\text{Co}_4\text{Cl}_4\text{O}_8$, $M = 1378.61$, monoclinic space group $\text{P}2(1)/c$, $a = 6.698(3)$, $b = 10.661(4)$, $c = 18.187(8)$ Å, $\beta = 90.375(5)^\circ$, $U = 1298.7(9)$ Å³, $Z = 1$, $\mu = 1.538\text{ mm}^{-1}$, 16473 reflections collected, $R_1 = 0.0382$ for 1795 $F > 4\sigma(F)$, $wR_2 = 0.1065$ and $\text{Goof} = 1.058$ for all 2639 data, 183 parameters, all non-hydrogen atoms anisotropic.

Data were collected on a Bruker SMART diffractometer ($\lambda = 0.71073$ Å) and the structures solved and refined using SHELXS and SHELXL.¹⁰ CCDC 209263 and 209264. See <http://www.rsc.org/suppdata/cc/b3/b304841a/> for crystallographic data in .cif or other electronic format.

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