

The Synthesis and Structure of a New Cobalt–Sodium Mixed-metal Two-dimensional Polymer

Alexander J. Blake, Liam M. Gilby and Richard E. P. Winpenny*

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK

Refluxing cobalt(II) nitrate with sodium acetate in acetic acid–ethanol leads to the formation of a novel mixed-metal polymer, which has been characterised by X-ray crystallography.

Several groups have been exploring synthetic routes to mixed-metal complexes using simple, ambidentate bridging ligands.^{1–3} Our strategy^{4–6} has used derivatives of 2-hydroxypyridine to produce a series of mixed-metal complexes. However, on characterising these complexes it became apparent that within these molecules μ_2 and μ_3 oxygen bridges were ubiquitous, sometimes bridging like metal atoms, sometimes unlike. It therefore seemed sensible to investigate even simpler ligand systems such as carboxylates to see if these

ligands would also support mixed-metal compounds. Here we report initial results of this approach.

Hydrated cobalt(II) nitrate and sodium acetate were mixed in a 1 : 4 mol ratio in a 50 : 50 ethanol–acetic acid solution. The pink solution was refluxed for 1 h, during which time it became deep purple. The solution was filtered, evaporated to dryness then refluxed in methanol for 15 min. Crystals suitable for X-ray analysis were grown by diethyl ether diffusion into a methanol solution. A similar reaction occurs

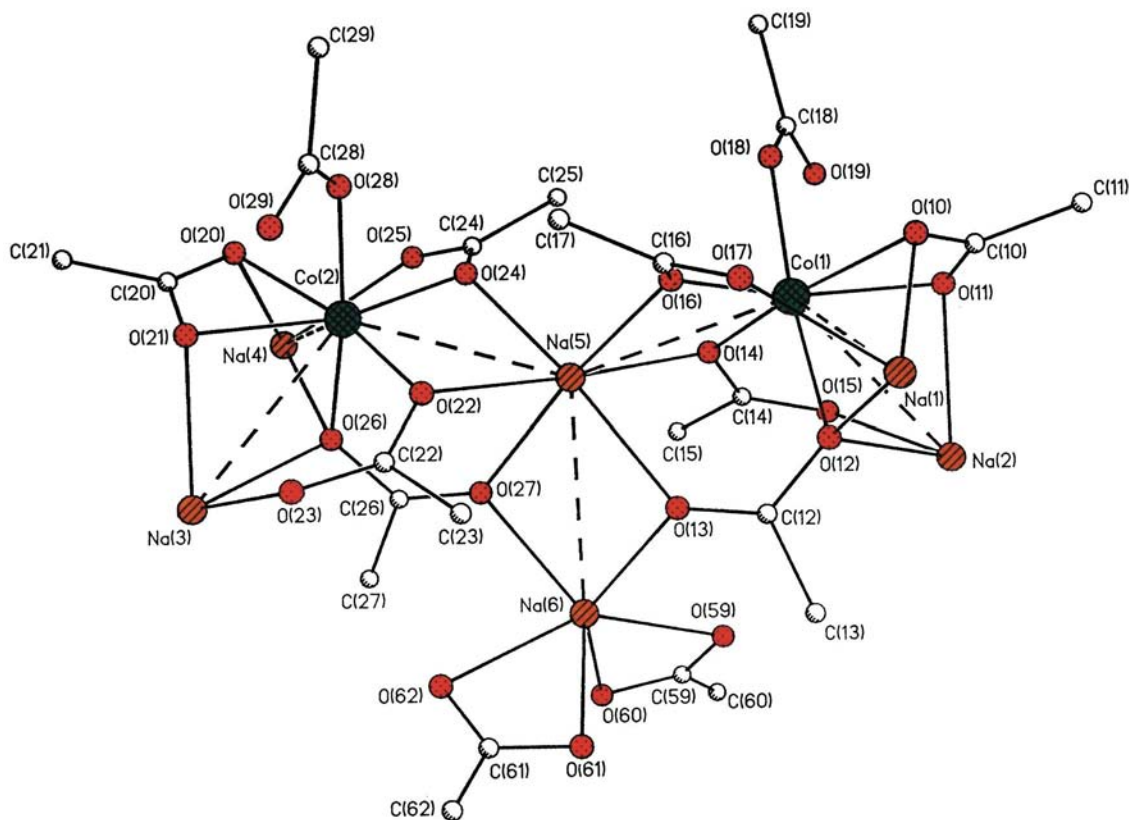


Fig. 1 A view of the first of two ' Co_2Na_6 ' units. The bond length ranges are: Co–O 2.026 to 2.305; Na–O 2.209 to 2.559 Å. Metal–metal contacts shown as dotted lines: Co–Na 3.219 to 3.353; Na–Na 3.187 to 3.366 Å.

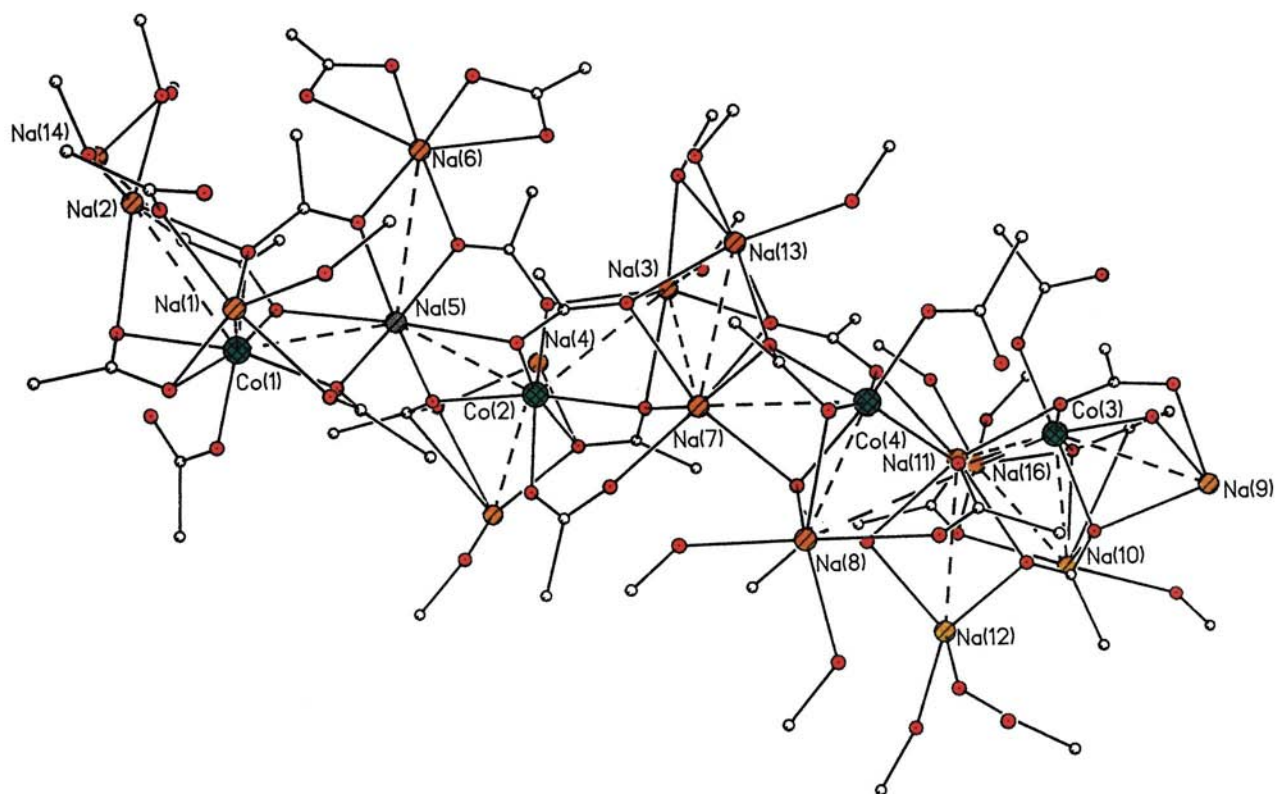


Fig. 2 A view of the complete asymmetric unit, illustrating the inter-unit linkage *via* Na(13)

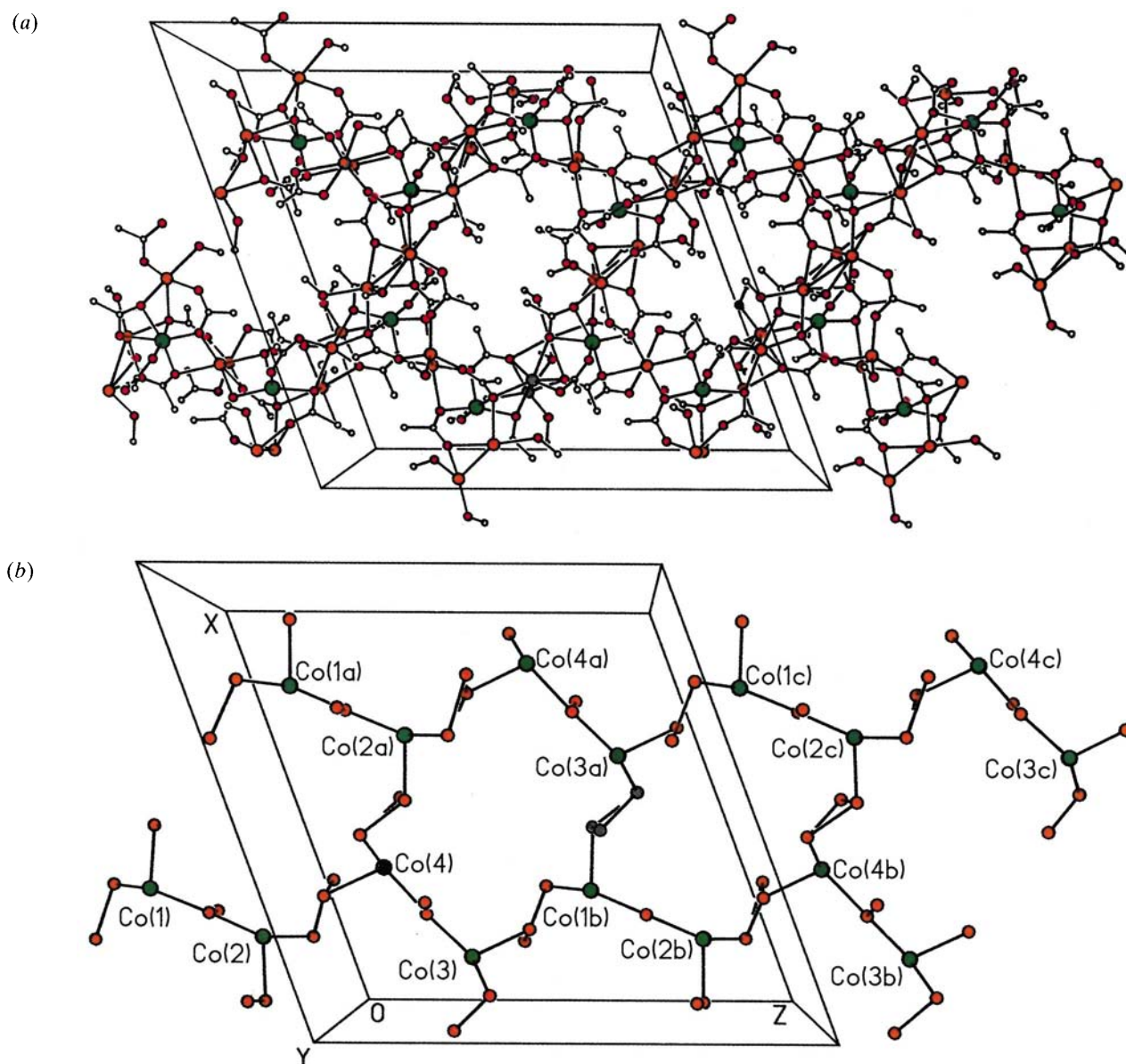


Fig. 3 (a) The two-dimensional polymer viewed down the *b* axis. (b) A schematic of the polymer, allowing the contiguous macrocyclic structure to be related to the Co_2Na_6 units, bridged *via* Na 'triangles'.

when anhydrous cobalt(II) chloride is used in place of cobalt nitrate.

X-Ray structural analysis† reveals an extraordinary mixed-metal two-dimensional polymer of stoichiometry $[\text{Co}_4\text{Na}_{16}(\text{O}_2\text{CMe})_{23}(\text{NO}_3)(\text{MeOH})_{15}]\cdot\text{MeOH}$. The structure is complicated and is best approached by discussing the

compound in terms of ' Co_2Na_6 ' units (the asymmetric unit containing two such units), and four Na atoms, which are involved in linking these Co_2Na_6 blocks *via* triangles of Na atoms. It might be felt that this division is somewhat arbitrary, but it is necessary to convey any information about the structural motifs in this unusual compound. All the cobalt atoms in the structure are in the 2+ oxidation state.

The first of the two closely similar Co_2Na_6 units is shown in Fig. 1. Each cobalt atom is bonded to six oxygen atoms which come from five acetates, of which one is bidentate and four monodentate towards the cobalt. In addition all these acetates bridge to Na atoms, chiefly to those within the Co_2Na_6 unit. Thus, both oxygens of the chelating acetates are μ_3 -bridging, *e.g.* O(10) binds to Na(1), while O(11) binds to Na(2) within the unit (see Fig. 1), and additionally each oxygen binds to a sodium outside the unit. One of the monodentate acetates is also pentanuclear, *e.g.* O(12) is bound to Co(1), Na(1) and Na(2), while O(13) bridges Na(5) and Na(6) (Fig. 1). Two are tetranuclear, binding to three metals within the Co_2Na_6 unit, *e.g.* O(16) is bound to Co(1) and Na(5), while O(17) is bound to Na(1) (Fig. 1), and one sodium outside the unit. The final acetate is bound only to a cobalt within a Co_2Na_6 unit, with the second oxygen binding to sodiums not in the unit.

† *Crystal data* for $\text{C}_{62}\text{H}_{133}\text{Co}_4\text{NNa}_{16}\text{O}_{65}$: $M = 2536$, monoclinic, space group $P2_1/n$, $a = 21.760(11)$, $b = 25.559(12)$, $c = 22.101(8)$ Å, $\beta = 110.34(3)^\circ$, $V = 11525$ Å³ [from 2θ values of 17 reflections measured at $\pm\omega$ ($25 \leq 2\theta \leq 26^\circ$)], $\lambda = 0.71073$ Å], $Z = 4$, $D_c = 1.46$ g cm⁻³, $T = 150$ K, pink tablet, $\mu = 0.71$ mm⁻¹. *Data collection and processing*: Stoë STADI-4 four-circle diffractometer, graphite-monochromated Mo-Kα X-radiation, ω scans. The structure was solved by the heavy-atom method. The data were corrected for absorption and refined with all non-carbon and non-hydrogen atoms anisotropic to give: $R = 0.0737$ ($R_w = 0.0822$) for 7450 independent observed reflections [$2\theta \leq 45^\circ$, $F > 2\sigma(F)$]. All calculations used SHELX76 (G. M. Sheldrick, University of Cambridge, England, 1976) or SHELXS-86 (G. M. Sheldrick, University of Göttingen, Germany, 1986). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

There are three types of Na atom within each Co_2Na_6 fragment. The first type of sodium [Na(5) in Fig. 1; Na(11) in the second unit], lies at the centre of the moiety, and its coordination sphere consists entirely of μ_2 -oxygens; two shared with one Co, two with the second and two O atoms shared with the second type of sodium in the unit [Na(6) in Fig. 1; Na(12) in the second fragment]. These two central sodiums, taken with the two cobalts form a distorted T.

The third type of sodium in the Co_2Na_6 unit are the four sodiums which lie at the extremities of the unit [Na(1) to Na(4) in Fig. 1]. These sodiums are involved in the inter-unit linkages, which lead to the polymeric structure, for in addition to intra-unit bonds to acetates, these Na atoms form bonds to oxygens from acetates in the other Co_2Na_6 fragment.

The two Co_2Na_6 units account for 16 of the 20 metals in the asymmetric unit. The four remaining sodium atoms [Na(13) to Na(16)] are involved in linking the Co_2Na_6 moieties. All four perform a similar function, and Fig. 2 illustrates the linkage via Na(13). Na(13) binds to two oxygens from the first Co_2Na_6 unit and one from the second. For Na(14), Na(15) and Na(16) the numbers of oxygens from each unit are: one and three, two and three, and two and two, respectively. For each such sodium a final coordination number of six is achieved by binding of solvent molecules. Each of these sodiums has close contacts (*ca.* 3.2 Å) to two of the third type of sodium from two different Co_2Na_6 units. This leads to triangles of sodiums within the links between Co_2Na_6 blocks.

This inter-unit linking leads to the formation of a two-dimensional polymer extending in the *ac* plane [Fig. 3(a)]. The exterior of each layer consists of methyl groups from acetate and methanols, and there are, therefore, no specific bonding interactions between layers. The layers consist of contiguous 24-membered macrocyclic rings, with 6 Na, 12 O

and 6 C atoms in the macrocycle. The 'walls' of the macrocycles are several atoms thick and contain the remaining metal atoms. The 'cavities' of the macrocycles are occupied by methyl groups derived from both acetate and methanol ligands. Fig. 3(b) is a schematic diagram that illustrates how this complex structure is built from the linking of Co_2Na_6 units via Na triangles.

Many of these structural features are highly unusual, for example, the presence of tri-, tetra- and penta-nucleating acetates in one structure, or the variety of means by which the disparate metal atoms are bridged. However, it is the overall structure that is most intriguing, illustrating how a spectacular mixed-metal polymer can be constructed from the simplest of ingredients.

We thank the SERC for a research studentship (to L. M. G.).

Received, 19th June 1992; Com. 2/03242B

References

- 1 S. Wang, G. Garzon, C. King, J.-C. Wang and J. P. Fackler, Jr., *Inorg. Chem.*, 1989, **28**, 4623.
- 2 M. S. Davidson, S. C. Llewellyn, M.-I. L. Solera, P. R. Raithby, R. Snaith and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1992, 573 and references cited therein.
- 3 L. H. Carrad, D. M. L. Goodgame and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1991, 175 and references cited therein.
- 4 A. J. Blake, P. E. Y. Milne, P. Thornton and R. E. P. Winpenny, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1139.
- 5 A. J. Blake, R. O. Gould, P. E. Y. Milne and R. E. P. Winpenny, *J. Chem. Soc., Chem. Commun.*, 1991, 1453.
- 6 A. J. Blake, R. O. Gould, P. E. Y. Milne and R. E. P. Winpenny, *J. Chem. Soc., Chem. Commun.*, 1992, 522.