Synthesis and crystal structure of the two-dimensional polymer $K_3Co(CN)_6{\cdot}2Rh_2(O_2CMe)_4$

Jian Lu, William T. A. Harrison and Allan J. Jacobson*

Department of Chemistry, University of Houston, Houston, TX 77204-5641, USA

The two-dimensional coordination polymer $K_3Co(CN)_6{\cdot}2Rh_2(O_2CMe)_4$, with a square lattice forms on reaction of an aqueous solution of $K_3Co(CN)_6$ with a thf solution of $Rh_2(O_2CMe)_4$.

The synthesis of coordination polymers is currently of interest as a route to microporous solids.[1] One approach has used metal cyanide compounds connected by organotin ligands to form polymeric materials that can contain large empty spaces.[2] Compounds with $Co(CN)_6^{3-}$ are among the best known, for example, $(Me_3Sn)_3Co(CN)_6$ and $(Me_3Pb)_3Co(CN)_6$.[2] Organic cyano ligands have also been widely used to form extended structures with inorganic/organometallic compounds.[3] Simple metal cyanide compounds have the advantage of providing different coordination geometries. They can be linear [*e.g.* $Au(CN)_2^-$, $Ag(CN)_2^-$], planar [*e.g.* $M(CN)_4^{2-}$, M = Ni, Pd, Pt], octahedral [*e.g.* $Co(CN)_6^{3-}$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$], tetrahedral [*e.g.* $Cu(CN)_4^{3-}$], or even dodecahedral and square-antiprismatic [*e.g.* $Mo(CN)_8^{4-}$, $W(CN)_8^{4-}$].[4] One recent example is the formation of three-dimensional polymers by reaction of $Mo(CN)_8^{4-}$ and $W(CN)_8^{4-}$ with Me_3Sn^+.[5] In the $M(CN)_8(Me_3Sn)_4$ (M = Mo, W) compounds, the Mo and W atoms are square-antiprismatically coordinated and the structures contain large empty channels. In studying the structures formed by inorganic compounds with organic cyano ligands, we noted the diversity of the reactions of tcne (tetracyanoethylene) with dirhodium acetate adducts. Tcne forms a two-dimensional sheet with $Rh_2(O_2CCF_3)_4$[6] or bridges two $Rh_2(O_2CMe)_4$ units in either 1,1 or *trans*-1,2 mode.[7] $Rh_2(O_2CMe)_4$ also forms polymeric compounds with other nitrogen donor ligands.[8] To investigate whether metal cyanides could be used to mimic the organic cyano ligands in reactions with dirhodium acetate, we have studied the reaction of $K_3Co(CN)_6$ with $Rh_2(O_2CMe)_4$. Here we report the synthesis and the structure of the two-dimensional $K_3Co(CN)_6{\cdot}2Rh_2(O_2CMe)_4$ compound that is formed.

When a green-blue thf solution of $Rh_2(O_2CMe)_4(MeOH)_2$ and a clear aqueous solution of $K_3Co(CN)_6$ were allowed to slowly interdiffuse, purple crystals of $K_3Co(CN)_6{\cdot}2Rh_2(O_2CMe)_4$ **1** formed directly at the interface. Reaction of the starting materials in thf–water gave **1** in quantitative yield. In contrast, mixing an acetonitrile solution of $Rh_2(O_2CMe)_4(MeOH)_2$ (purple) with an aqueous solution of $K_3Co(CN)_6$ (colourless) resulted in a homogeneous purple solution and no precipitate. Upon evaporating most of the solvent, a purple precipitate formed and was shown by X-ray powder diffraction to be identical to **1**. The large amount of the stronger donor ligand acetonitrile competes with $Co(CN)_6^{3-}$ in coordinating to $Rh_2(O_2CMe)_4$. The purple colour of an acetonitrile solution of $Rh_2(O_2CMe)_4$, compared to the green-blue thf solution, is also a strong indication that the axial position of $Rh_2(O_2CMe)_4$ is blocked by acetonitrile.[9] Compound **1** is insoluble in most solvents including water, methanol, ethanol, acetone, thf, and acetonitrile but dissolves in strong coordinating solvents such as pyridine and Me_2SO. When **1** is dissolved in strong coordinating solvents, such as pyridine and Me_2SO, it is very likely that solvent molecules coordinate to the dirhodium centre and the linkage between $Co(CN)_6^{3-}$ and $Rh_2(O_2CMe)_4$ is broken.

Unlike the black compound formed by tcne with $Rh_2(O_2CCF_3)_4$,[6] **1** has the typical purple colour of dirhodium complexes with nitrogen donor ligands.[10] In the corresponding tcne compounds, tcne acts both as a strong electron acceptor and as a ligand. The CN stretching bands in tcne$\cdot$ $2Rh_2(O_2CCF_3)_4$ are red shifted from those in tcne due to the π interaction between tcne and $Rh_2(O_2CCF_3)_4$.[6] In $K_3Co(CN)_6{\cdot}2Rh_2(O_2CMe)_4$, the cobalt cyanide acts as a simple σ donor to dirhodium acetate and the CN stretching modes observed in the IR spectrum at 2147 and 2126 cm^{-1} are blue shifted from those in $K_3Co(CN)_6$ (2129, 2087 cm^{-1}).

The structure of **1** is closely packed with a mean volume per atom of 17.3 $Å^3$.[†] Each $Co(CN)_6^{3-}$ unit uses four in-plane CN groups to connect to $Rh_2(O_2CMe)_4$ dimers *via* Co–C–N–Rh bonds, thus forming a two-dimensional sheet. The two remaining apical CN bond to K^+ cations. The layer containing the cobalt and rhodium atoms is almost square with *cis* C–Co–C angles of 88.9(7) and 91.1(7)°. The anionic $[Co(CN)_6{\cdot}2Rh_2(O_2CMe)_4]^{3-}$ layers are stacked along the *c* axis and the distance between two adjacent layers is 6.65 Å. The acetate groups bridging the dirhodium centres are disordered. One set of acetate groups is eclipsed with respect to the four Co–CN bonds that lie in a plane perpendicular to the layer and the other set are staggered with respect to Co–CN bonds. Fig. 1 shows the local coordination of $Co(CN)_6$ and $Rh_2(O_2CMe)_4$ units with only the eclipsed acetate groups shown. If all of the acetate groups were eclipsed, the closest contact of carbon atoms on the methyl groups (O_2CMe) that lie close to the Co–Rh plane would be 2.72 Å which is sterically unfavourable. If all of the acetate groups were staggered, the closest contact of carbon atoms on methyl groups between the layers would be 1.14 Å. Such close

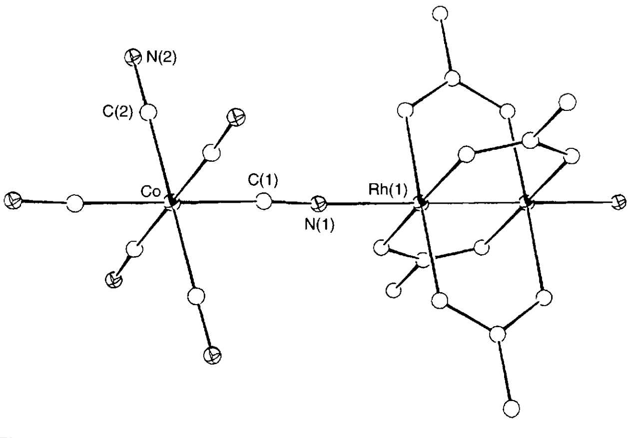

Fig. 1 ORTEP drawing of the local coordination of **1**. The staggered acetate groups are removed for clarity. Selected bond distances (Å) and angles (°): Rh(1)–Rh(1) 2.397(2), Rh(1)–N(1) 2.20(1), Co–C(1) 1.89(1), Co–C(2) 1.87(2), C(1)–N(1) 1.15(2), C(2)–N(2) 1.13(3); Rh(1)–Rh(1)–N(1) 178.8(3), Rh(1)–N(1)–C(1) 177.1(10), Co–C(1)–N(1) 176.1(11), Co–C(2)–N(2) 176.2(17), C(2)–Co–C(2) 180, C(1)–Co–C(1) 180, C(1)–Co–C(1) 91.1(7).

contacts can be avoided if we keep the mirror symmetry in *C*2/*m* and remove the twofold axis [Fig. 2(*a*)]. A refinement of the data in space group *Cm* did not, however, resolve the disorder problem. Fig. 2(*b*) shows another possible arrangement that also prevents close contacts. In this structure, the acetate groups alternate in the rectangle between eclipsed and staggered. Structure 2(*b*) can in principle also resolve the disorder but only in the triclinic space group *C*1. Alternatively, the structure may consist of a disordered arrangement of both 2(*a*) and 2(*b*) types of layers.

The Rh–Rh [2.397(2) Å] and Rh–N distances [2.20(1) Å] in **1** are similar to those of other $Rh_2(O_2CMe)_4L_2$ compounds.[10]

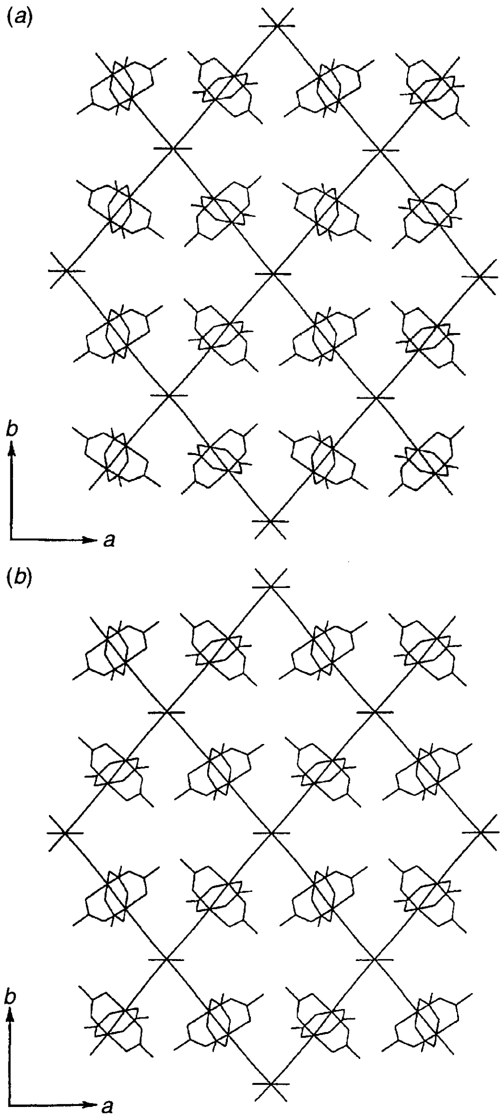

Fig. 2 Network view of the structure of **1** along the *c* axis (*a*) with the acetate groups related by the mirror plane perpendicular to the *b* axis eclipsed and the acetate groups related by the twofold axis along *b* staggered, (*b*) the acetate groups alternate between eclipsed and staggered in one square

The structure of **1** is comparable to that of the two-dimensional polymer $[Rh_2(O_2CCF_3)_4]_2(tcne)(C_6H_6)_2$.[6] In the tcne structure, the acetate groups are alternately eclipsed and staggered in an ordered arrangement. In **1**, the $Co(CN)_6^{3-}$ group acts like tcne in tcne·$2Rh_2(O_2CCF_3)_4\cdot 2C_6H_6$ except that it provides the possibility of coordination along the third direction. Due to the bulky size of $Rh_2(O_2CMe)_4$, however, steric interference between the acetate groups prevents the formation of a three-dimensional polymer. The synthesis of the three-dimensional analogue may be possible using a smaller bridging group, for example HCO_2^- in $Rh_2(O_2CH)_4$.

This material is based in part on work supported by the Texas Advanced Research Program under grant no. 003652-048. We also thank the Robert A. Welch Foundation for support of this work and Dr James Krop for help with crystallography.

Footnote

† *Crystal data* for **1**: purple, parallelepiped crystal, size 0.10 × 0.15 × 0.18 mm, space group *C*2/*m* (no. 12), a = 16.354(7), b = 18.379(5), c = 7.908(3) Å, β = 111.61(3)°, U = 2210(2) Å^3, Z = 2, D_c = 1.83 g cm^{-3}, μ(Mo-Kα) = 25.5 cm^{-1}. The unit-cell constants were optimized by least-squares refinement based on 21 reflections in the range 18 < 2θ < 24°. Intensity data were collected on a Simens/Nicolet automated four-circle diffractometer (graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å) at −50(2) °C in the ω–2θ scanning mode. 1613 intensity data measured in the range 4 < 2θ < 45°; 1052 observed reflections with $I > 3\sigma(I)$; no crystal decay. The acetate groups bridging the rhodium atoms are disordered; a refinement indicated almost equal occupancy for both positions. Both potassium cation sites are half occupied. Final R = 0.0646 and R_w = 0.0706, 108 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 M. D. Ward, *Nature*, 1995, **374**, 764; G. B. Gardener, D. Venkataraman, J. S. Moore and S. Lee, *Nature*, 1995, **374**, 792 and references therein.

2 A. K. Brimah, E. Siebel, R. D. Fischer, D. A. Davies, D. C. Apperley and R. B. Harris, *J. Organomet. Chem.*, 1994, **475**, 85; U. Behrens, A. K. Brimah, T. M. Soliman, R. D. Fischer, D. C. Apperley, N. A. Davies and R. K. Harris, *Organometallics*, 1992, **11**, 1718 and references therein.

3 See for example: D. T. Cromer and A. C. Larson, *Acta Crystallogr., Sect. B*, 1972, **28**, 1052; L. Shields, *J. Chem. Soc., Faraday Trans. 2*, 1985, **81**, 1; B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1989, **111**, 5962.

4 W. P. Griffith, *Coord. Chem. Rev.*, 1975, **17**, 177.

5 J. Lu, W. T. A. Harrison and A. J. Jacobson, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2557.

6 F. A. Cotton and Y. Kim, *J. Am. Chem. Soc.*, 1993, **115**, 8511.

7 F. A. Cotton, Y. Kim and J. Lu, *Inorg. Chim. Acta*, 1994, **221**, 1.

8 For example: C. A. Crawford, E. F. Day, W. E. Streib, J. C. Huffman and G. Christou, *Polyhedron*, 1994, **13**, 2933; K. Aoki and H. Yamazaki, *J. Am. Chem. Soc.*, 1984, **106**, 3691.

9 F. A. Cotton and J. L. Thompson, *Acta Crystallogr., Sect. B*, 1981, **37**, 2235.

10 F. A. Cotton and R. A. Walton, *Multiple Bonds between Metal Atoms*, 2nd edn., Clarendon Press, Oxford, 1993.

Received, 18th September 1995; Com. 5/06120B