Inorganica Chimica Acta, 221 (1994) 1–4

Inorganica Chimica Acta
Preliminary Communication

$[Rh_2(O_2CCH_3)_4TCNE]_x$ polymers: isomers with either 1,1- or *trans*-1,2-TCNE bridges

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(Received January 13, 1994)

Abstract

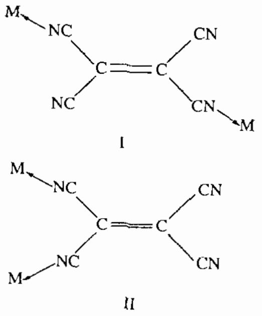
Two different polymeric solids have been obtained by the reaction of $Rh_2(O_2CCH_3)_4$ with TCNE (tetracyanoethylene). Both contain infinite chains, $[Rh_2(O_2CCH_3)_4(TCNE)_\infty$, with solvent molecules (benzene and *m*-xylene) occupying interstices. In compound **1** the TCNE units serve as 1,1-bridges while in the other, **2**, they serve as *trans*-1,2-bridges. Both compounds are black.

Key words: Crystal structures; Rhodium compounds; Tetracyanoethylene compounds; Polymeric compounds

Introduction

The ability of TCNE (tetracyanoethylene) to use two or more of its CN groups as donors to metal atoms, thereby forming chains [1] or nets [2], has already been established. It is, of course, known that when more than two metal atoms are attached to one TCNE, vicinal CN groups, of necessity, function as donors. However in all previous cases where TCNE employs only two CN groups as donors, so as to form chains, these CN groups are employed in a *trans*-1,2-fashion (I).

We now report that while $Rh_2(O_2CCH_3)_4$ and TCNE interact to form a chain compound incorporating 1,2-TCNE units, it is also possible by a different choice of preparative conditions, to obtain a second $[Rh_2(O_2CCH_3)_4(TCNE)]_x$ chain compound in which there are 1,1-TCNE bridges, as shown schematically in II (Scheme 1).



Scheme 1.

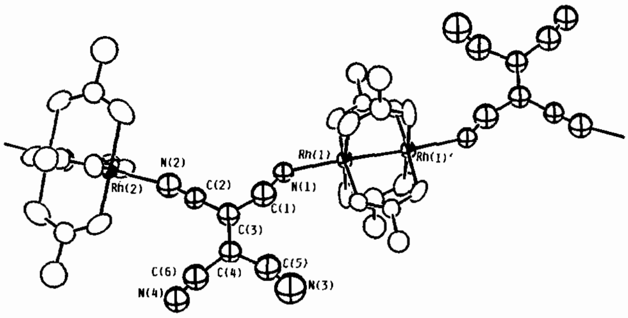


Fig. 1. A portion of the infinite chain in compound **1**.

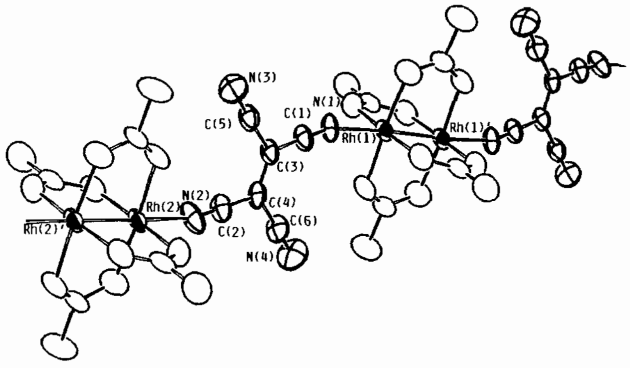


Fig. 2. A portion of the infinite chain in compound **2**.

Experimental

Preparation

The starting material, $Rh_2(O_2CCH_3)_4(CH_3OH)_2$, was prepared by using a literature procedure [3]. Tetracyanoethylene (TCNE) was purchased from TCI America Company and used as received.

$Rh_2(O_2CCH_3)_4(CH_3OH)_2$ (51 mg, 0.10 mmol) was dissolved in 5 ml of THF. A solution of TCNE, 13 mg (0.1 mmol) in 5 ml of benzene, was added to this solution. Evaporating solvent from the solution mixture provided beautiful crystals of $Rh_2(O_2CCH_3)_4$(1,1-TCNE) (**1**). The $Rh_2(O_2CCH_3)_4$(1,2-TCNE) compound (**2**) was obtained by a slightly different procedure. The same solution mixture described above was covered by a layer of hexanes, which slowly diffused into the mixture.

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SSDI 0020-1693(94)03971-P

TABLE 1. Crystal data for $Rh_2(CH_3COO)_4$(1,1-TCNE)·C_6H_6 (**1**) and $Rh_2(CH_3COO)_4$(*trans*-1,2-TCNE)·(C_6H_6)(C_8H_{10}) (**2**)

	1	**2**
Formula	$Rh_2O_8N_4C_{20}H_{18}$	$Rh_2O_8N_4C_{28}H_{28}$
Formula weight	648.20	754.37
Space group	*Pbcn* (No. 60)	$P2_1/c$ (No. 14)
a (Å)	16.710(1)	11.406(1)
b (Å)	21.454(2)	21.615(4)
c (Å)	16.410(2)	12.886(1)
α (°)	90.0	90.0
β (°)	90.0	95.521(7)
γ (°)	90.0	90.0
V (Å^3)	5883(1)	3162(1)
Z	8	4
D_{calc} (g/cm^3)	1.464	1.584
Crystal size (mm)	0.32×0.38×0.10	0.32×0.38×0.42
μ(Cu Kα) (cm^{-1})	96.610	90.728
Data collection instrument	AFC5R Rigaku	AFC5R Rigaku
Radiation monochromated in incident beam (Cu Kα, Å)	1.54184	1.54184
Orientation reflections: no.; range (°)	24; $33<2\theta\leqslant 51$	20; $38<2\theta\leqslant 46$
Temperature (°C)	20	20
Scan method	2θ–ω	2θ–ω
Data collection range, 2θ (°)	$4\leqslant 2\theta\leqslant 120$	$4\leqslant 2\theta\leqslant 120$
No. unique data, total with $F_o^2>3\sigma(F_o^2)$	4385, 1740	4715, 3503
No. parameters refined	187	379
Transmission factors: max., min.	1.00, 0.32	1.00, 0.71
R^a	0.115	0.065
R_w^b	0.154	0.091
Quality-of-fit indicator^c	3.576	2.426
Largest shift/e.s.d., final cycle	0.01	0.01
Largest peak (e/Å^3)	4.228	1.822

$^aR=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^bR_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w=1/\sigma^2(|F_o|)$. ^{c}Quality-of-fit $=[\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{param})]^{1/2}$.

This procedure did not give any crystals. However, after the mixture of hexanes, which also contained some *m*-xylene, had diffused into the mixture, slow evaporation of solvent gave crystals of the $Rh_2(O_2CCH_3)_4$(1,2-TCNE) compound (**2**). The crystals of both compounds were black and it was not until the structures were determined that it was clear that they are different.

X-ray crystallography

Black crystals of each $Rh_2(O_2CCH_3)_4$TCNE compound were mounted on glass fibers. Data were collected on a AFC5R Rigaku diffractometer at 20 °C employing Cu Kα radiation. The determination of the crystal systems, data collection procedures, structure solutions and refinements were all carried out by procedures that have been described before [4, 5].

The unit cell of **1** was shown to be orthorhombic on the basis of 24 reflections in the range $33<2\theta<51°$. The space group was uniquely determined as *Pbcn* (No. 60) on the basis of the systematic absences. The unit cell of **2** was determined to be monoclinic on the basis of 20 reflections in the range $38<2\theta<46°$. The space group was determined as $P2_1/c$ (No. 14). Corrections were applied [6]. There was no significant decay during either of the data collections. Crystallographic details are summarized in Table 1.

In each case a Patterson map revealed the positions of two independent rhodium atoms. The positions of the other non-hydrogen atoms were obtained by an alternating sequence of difference Fourier maps and least-square refinements. For **1**, all carbon and nitrogen atoms were refined with isotropic thermal parameters and the rhodium and the oxygen atoms were refined with anisotropic thermal parameters. Many crystals of **1** were examined but, unfortunately, all those that diffracted well were twinned and data had to be collected on a crystal that was untwinned but of inferior quality. Efforts to obtain better data are continuing, however, and we hope to obtain a more satisfactory refinement in the future. For **2**, all atoms were refined with anisotropic thermal parameters. The atomic positional parameters of **1** and **2** are given in Tables 2 and 3, respectively.

TABLE 2. Positional parameters and their e.s.d.s for $Rh_2(O_2CCH_3)_4(1,1\text{-}TCNE)\cdot C_6H_6$ (**1**)

Atom	*x*	*y*	*z*	*B* (Å^2)
Rh(1)	0.0125(2)	0.4452(1)	0.0033(1)	3.02(5)
Rh(2)	0.0172(2)	0.0530(1)	0.0098(1)	3.39(5)
O(11)	−0.038(2)	0.444(1)	0.114(1)	5.5(6)
O(12)	0.122(1)	0.467(1)	0.053(1)	3.7(5)
O(13)	0.068(2)	0.453(1)	−0.108(1)	5.4(6)
O(14)	−0.093(1)	0.431(1)	−0.047(1)	4.7(6)
O(21)	0.066(1)	0.031(1)	0.118(1)	3.9(5)
O(22)	−0.094(1)	0.064(1)	0.064(1)	4.8(6)
O(23)	−0.038(1)	0.072(1)	−0.101(1)	4.9(6)
O(24)	0.121(1)	0.036(1)	−0.050(1)	3.9(5)
N(1)	0.041(2)	0.344(1)	0.017(1)	3.6(5)*
N(2)	0.053(2)	0.149(2)	0.034(2)	5.6(7)*
N(3)	0.228(2)	0.353(2)	0.200(2)	9(1)*
N(4)	0.240(2)	0.163(2)	0.213(2)	5.8(8)*
C(1)	0.074(3)	0.310(2)	0.051(2)	6(1)*
C(2)	0.079(2)	0.194(2)	0.054(2)	3.9(7)*
C(3)	0.109(2)	0.251(2)	0.081(2)	4.6(7)*
C(4)	0.170(2)	0.253(2)	0.139(2)	4.5(7)*
C(5)	0.199(3)	0.316(2)	0.163(2)	6(1)*
C(6)	0.204(3)	0.196(2)	0.180(2)	6(1)*
C(11)	−0.064(2)	0.493(2)	0.141(2)	4.4(8)*
C(12)	0.139(2)	0.523(2)	0.062(2)	2.9(6)*
C(13)	−0.100(2)	0.494(2)	0.228(2)	5.5(9)*
C(14)	0.225(2)	0.533(2)	0.097(2)	4.0(8)*
C(21)	0.066(2)	−0.027(2)	0.137(2)	4.0(7)*
C(22)	−0.131(2)	0.017(2)	0.074(2)	3.7(7)*
C(23)	0.105(3)	−0.047(2)	0.219(2)	7(1)*
C(24)	−0.213(2)	0.031(2)	0.114(2)	5.3(9)*
C(61)	0.671(4)	0.196(3)	0.504(3)	9(2)*
C(62)	0.671(3)	0.267(3)	0.489(3)	9(1)*
C(63)	0.711(3)	0.309(2)	0.522(3)	7(1)*
C(64)	0.780(3)	0.292(3)	0.580(3)	10(2)*
C(65)	0.781(3)	0.236(3)	0.601(3)	9(1)*
C(66)	0.731(4)	0.184(3)	0.557(3)	10(2)*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

TABLE 3. Positional parameters and their e.s.d.s for $Rh_2(O_2CCH_3)_4$(*trans*-1,2-TCNE)$\cdot(C_6H_6)(C_8H_{10})$ (**2**)

Atom	*x*	*y*	*z*	*B* (Å^2)
Rh(1)	0.98083(5)	0.05326(3)	0.01275(5)	3.00(1)
Rh(2)	0.52564(5)	0.44681(3)	0.00497(5)	3.05(1)
O(1)	0.9578(5)	−0.0427(3)	−0.1643(5)	4.5(1)
O(2)	0.8195(5)	0.0276(3)	0.0504(5)	4.4(1)
O(3)	0.9214(5)	0.0580(2)	−0.1407(5)	4.5(1)
O(4)	1.1445(5)	0.0724(3)	−0.0276(5)	4.6(1)
O(21)	0.3132(5)	0.5279(3)	0.0336(4)	4.0(1)
O(22)	0.4228(5)	0.5394(3)	0.8405(5)	4.3(1)
O(23)	0.3626(5)	0.4279(3)	0.0444(5)	4.5(1)
O(24)	0.4716(5)	0.4392(3)	0.8515(5)	4.5(1)
N(1)	0.9320(6)	0.1501(3)	0.0314(5)	3.8(1)
N(2)	0.5790(6)	0.3499(3)	0.0106(6)	4.7(2)
N(3)	0.9277(8)	0.3506(4)	0.0333(7)	5.9(2)
N(4)	0.5760(8)	0.1455(4)	0.0120(7)	6.3(2)
C(1)	0.8788(7)	0.1932(3)	0.0300(6)	3.7(2)
C(2)	0.6258(8)	0.3043(4)	0.0146(6)	3.7(2)
C(3)	0.8104(7)	0.2494(3)	0.0259(6)	3.4(2)
C(4)	0.6920(8)	0.2482(3)	0.0173(6)	3.3(2)
C(5)	0.8748(7)	0.3062(4)	0.0291(7)	3.8(2)
C(6)	0.6270(8)	0.1903(4)	0.0141(7)	4.2(2)
C(10)	0.8815(9)	0.0166(5)	−0.3099(7)	5.2(2)
C(11)	0.9240(6)	0.0106(4)	−0.1964(7)	3.8(2)
C(12)	0.7928(7)	−0.0281(4)	0.0529(7)	4.0(2)
C(20)	0.6738(9)	−0.0436(5)	0.0893(9)	6.4(3)
C(21)	0.2906(7)	0.4732(4)	0.0528(6)	4.1(2)
C(22)	0.4325(6)	0.4864(4)	0.8025(7)	4.2(2)
C(30)	0.1717(8)	0.4574(5)	0.0862(9)	6.6(3)
C(40)	0.3921(9)	0.4786(6)	0.6888(7)	5.9(3)
C(61)	0.7545(9)	0.1889(4)	0.2741(6)	5.3(2)
C(62)	0.8480(8)	0.2318(5)	0.2803(7)	4.9(2)
C(63)	0.8230(8)	0.2949(4)	0.2786(6)	4.4(2)
C(64)	0.709(1)	0.3152(4)	0.2675(8)	5.1(2)
C(65)	0.6159(9)	0.2750(5)	0.2623(7)	5.5(2)
C(66)	0.6383(9)	0.2104(5)	0.2644(7)	5.5(2)
C(67)	0.784(1)	0.1196(5)	0.2736(9)	9.8(4)
C(68)	0.486(1)	0.2980(7)	0.251(1)	9.8(4)
C(71)	0.161(1)	0.2057(6)	0.799(1)	9.7(4)
C(72)	0.157(1)	0.2471(7)	0.712(1)	10.2(5)
C(73)	0.189(1)	0.3067(7)	0.733(1)	10.4(5)
C(74)	0.232(1)	0.3244(6)	0.832(1)	11.1(5)
C(75)	0.242(2)	0.2861(7)	0.913(1)	11.8(5)
C(76)	0.202(1)	0.2252(6)	0.897(1)	9.8(4)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

Structure description

The chain structures of **1** and **2**, shown in Figs. 1 and 2, respectively, feature dirhodium units bridged by TCNE molecules into infinite chains through 1,1- or *trans*-1,2-cyano groups. In each one, two independent $Rh_2(O_2CCH_3)_4$ units have their midpoints on inversion centers. For **1**, the Rh(1)–Rh(1)′ and Rh(2)–Rh(2)′ distances are 2.3891(3) and 2.367(3) Å, respectively (Table 4). The axial Rh–N(TCNE) bonds have two crystallographic independent values, 2.24(3) and 2.19(3) Å. Benzene molecules occupy cavities between the chains. For *trans*-Rh_2-$(O_2CCH_3)_4$TCNE, the Rh(1)–Rh(1)′ and Rh(2)–Rh(2)′ distances are 2.3725(8) and 2.3730(8) Å, respectively (Table 5). The axial Rh–N(TCNE) bonds have two crystallographic independent values, 2.185(6) and 2.181(7) Å. Benzene and 1,3-xylene molecules occupy cavities between the chains. The presence of these interstitial solvent molecules results in the packing densities being normal, i.e. 21.6 and 18.8 Å^3/atom for **1** and **2**, respectively.

Results and discussion

The two compounds described here provided an unprecedented example of isomerism in TCNE–metal

TABLE 4. Selected bond distances (Å) and angles (°) for $Rh_2(O_2CCH_3)_4(1,1\text{-TCNE})\cdot C_6H_6$ (**1**)

Bond distances					
Rh(1)–Rh(1)	2.389(3)	N(2)–C(2)	1.09(5)	C(3)–C(4)	1.40(4)
Rh(1)–N(1)	2.24(3)	N(3)–C(5)	1.11(6)	C(4)–C(5)	1.50(6)
Rh(2)–Rh(2)	2.367(3)	N(4)–C(6)	1.08(5)	C(4)–C(6)	1.50(6)
Rh(2)–N(2)	2.19(3)	C(1)–C(3)	1.47(6)		
N(1)–C(1)	1.08(5)	C(2)–C(3)	1.40(6)		
Bond angles					
Rh(1)–Rh(1)–N(1)	176.2(7)	N(2)–C(2)–C(3)	178.(4)	C(3)–C(4)–C(6)	123.(4)
Rh(2)–Rh(2)–N(2)	176.7(8)	C(1)–C(3)–C(2)	120.(3)	C(5)–C(4)–C(6)	120.(3)
Rh(1)–N(1)–C(1)	146.(3)	C(1)–C(3)–C(4)	119.(4)	N(3)–C(5)–C(4)	159.(4)
Rh(2)–N(2)–C(2)	169.(3)	C(2)–C(3)–C(4)	121.(4)	N(4)–C(6)–C(4)	165.(4)
N(1)–C(1)–C(3)	164.(4)	C(3)–C(4)–C(5)	116.(4)		

Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE 5. Selected bond distances (Å) and angles (°) for $Rh_2(O_2CCH_3)_4(\textit{trans}\text{-}1,2\text{-TCNE})\cdot(C_6H_6)(C_8H_{10})$ (**2**)

Bond distances					
Rh(1)–Rh(1)	2.3725(8)	N(2)–C(2)	1.12(1)	C(3)–C(4)	1.34(1)
Rh(1)–N(1)	2.185(6)	N(3)–C(5)	1.13(1)	C(3)–C(5)	1.43(1)
Rh(2)–Rh(2)	2.3730(8)	N(4)–C(6)	1.13(1)	C(4)–C(6)	1.45(1)
Rh(2)–N(2)	2.181(7)	C(1)–C(3)	1.44(1)		
N(1)–C(1)	1.11(1)	C(2)–C(4)	1.43(1)		
Bond angles					
Rh(1)–Rh(1)–N(1)	175.7(2)	N(2)–C(2)–C(4)	176.2(9)	C(2)–C(4)–C(6)	117.6(8)
Rh(2)–Rh(2)–N(2)	177.6(2)	C(1)–C(3)–C(4)	121.4(7)	C(3)–C(4)–C(6)	121.7(7)
Rh(1)–N(1)–C(1)	161.1(6)	C(1)–C(3)–C(5)	116.6(7)	N(3)–C(5)–C(3)	178.4(8)
Rh(2)–N(2)–C(2)	167.8(7)	C(4)–C(3)–C(5)	121.9(7)	N(4)–C(6)–C(4)	179.5(9)
N(1)–C(1)–C(3)	178.7(9)	C(2)–C(4)–C(3)	120.7(7)		

Numbers in parentheses are e.s.d.s in the least significant digits.

chain compounds. At this time, because of poor crystal quality, the low accuracy of the dimensions of **1** does not allow any detailed discussion. For **2**, the Rh–N, N≡C, NC–C and C=C distances are practically the same as those previously reported for $[Rh_2(O_2CCF_3)_4]_2(TCNE)\cdot 2C_6H_6$ [2]. Thus, again, even though the Rh_2^{4+} core is now more electron-rich, there is structurally detectable transfer of electron density to the TCNE molecules. Nevertheless, the black color of both compounds indicates that strong charge transfer bands occur in the spectra. It is also notable that the change from $Rh_2(O_2CCF_3)_4$ to $Rh_2(O_2CCH_3)_4$, that is from a stronger to a weaker Lewis acid has not resulted in any significant change in the Rh–N distances, when **2** is compared to $[Rh_2(O_2CCF_3)_4]_2(TCNE)(C_6H_6)_2$.

Supplementary material

Additional data, available on request from author F.A.C., includes tables of anisotropic displacement parameters, complete lists of bond distances and angles, and lists of observed and calculated structure factors.

Acknowledgement

We thank the Texas Advance Research Program for financial support.

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