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LETTER

Metal–betaine interactions
Part V. Molecular and crystal structure of tetra(betaine)dichlorodirhodium(II) dichloride tetrahydrate, $[Rh_2(Me_3NCH_2CO_2)_4Cl_2]Cl_2 \cdot 4H_2O$[*]

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A large number of tetra(carboxylato)dimetal species having the general stoichiometry $M_2(RCO_2)_4L_2$, either neutral or charged, have been prepared and characterized by single-crystal X-ray analysis to investigate the nature of the metal–metal bonds in them [2, 3]. For a neutral dirhodium(II,II) compound belonging to this class, eight electrons fill the M–M σ, π and δ orbitals, whereas another six enter the δ^* and π^* orbitals giving a net Rh–Rh bond order of 1. This qualitative interpretation is consistent with the results of quantitative calculation by SSCF-Xα-SW [4] and molecular mechanics methods [5]. For a series of $Rh_2(RCO_2)_4L_2$ adducts with neutral L ligands occupying the axial positions, Christoph and Koh [6] discussed the *trans* influence and dependence of the Rh–Rh bond distance upon the nature of the axial ligands, and Cotton and Felthouse [7] also described the effects of the R group substituents and axial donor ligands on the Rh–Rh bond distance.

Recently we began to conduct a systematic study of the chemistry of betaine compounds $R_3\overset{+}{N}CH_2CO_2{}^{-}$[†], which can be used as neutral analogues of carboxylato ligands in the preparation of complexes with many metal ions [1, 8]. In the context of a tetra-bridged dinuclear system, the extent to which the metal–metal interaction is affected by varying the overall charge of the bridging and axial ligands needs to be answered. In this paper, we report the preparation and X-ray structure determination of the title dimeric rhodium(II) betaine complex, $[Rh_2(BET)_4Cl_2]Cl_2 \cdot 4H_2O$ (BET = $Me_3NCH_2CO_2$).

Experimental

Preparation of $[Rh_2(BET)_4Cl_2]Cl_2 \cdot 4H_2O$

A modification of the literature method for the preparation of bridged carboxylato complex was used [9]. Rhodium trichloride hydrate and excess betaine in absolute ethanol were gently refluxed under nitrogen for one day. The initial red solution slowly turned to green, and a green solid was deposited. The precipitate (100 mg) was dissolved in water–ethanol (1:1, *c.* 20 ml) and the solvent was allowed to evaporate slowly. After several days the title complex was obtained as well-formed plate-like crystals. Infrared spectra were recorded as Nujol mulls between KBr plates using a Nicolet 20SXC FT-IR spectrometer. The density of the crystals was determined by flotation in 1,2-dibromoethane/CCl_4.

Crystal data

$C_{20}H_{52}Cl_4N_4O_{12}Rh_2$, $M_r = 888.38$, monoclinic, $a = 11.040(3)$, $b = 14.881(4)$, $c = 11.139(2)$ Å, $\beta = 106.66(2)°$, $V = 1753.2(8)$ Å^3, $Z = 2$, $D_c = 1.683$ g cm^{-3}, $D_m = 1.690$ g cm^{-3}, $F(000) = 908$, $\lambda = 0.71069$ Å, μ(Mo Kα) = 12.89 cm^{-1}, space group $P2_1/c$ (No. 14).

X-ray data collection, structure solution and refinement

Raw intensities (5082 unique reflections) collected up to $2\theta_{max} = 55°$ on a Nicolet R3m/V diffractometer were processed with the profile-fitting procedure of Diamond [10] and corrected for absorption using ψ-scan data [11], of which 3725 with $I > 3\sigma(I)$ were considered observed and used in structure analysis. The structure was solved by Patterson superposition and refined with anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms of the BET ligands were generated geometrically (C–H bonds fixed at 0.96 Å) and assigned the same isotropic temperature factor of $U = 0.08$ Å^2. Final R and R_w are 0.035 and 0.043 with $w = [\sigma^2(F_o) + 0.0002|F_o|^2]^{-1}$. Computations were performed using the SHELTXL-PLUS program package [12] on a DEC MicroVAX-II computer. Analytic expressions of atomic scattering

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[†] The IUPAC name of the archetypal betaine, $Me_3NCH_2CO_2$ (abbreviated as BET), is 1-carboxy-*N*,*N*,*N*-trimethylmethanaminium hydroxide inner salt.

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TABLE 1. Atomic coordinates (×10^5 for Rh; ×10^4 for other atoms) and equivalent isotropic temperature factors (Å^2×10^4 for Rh and Cl; ×10^3 for other atoms)

Atom	x	y	z	U_{eq}^{a}
Rh(1)	5189(2)	2086(2)	42241(2)	260(1)
Cl(1)	1733(1)	689(1)	2690(1)	457(3)
O(1)	−799(2)	1122(2)	6014(2)	36(1)
O(2)	153(3)	1513(2)	4548(2)	37(1)
O(3)	1206(2)	−146(2)	7088(2)	39(1)
O(4)	2167(2)	233(2)	5634(2)	38(1)
N(1)	−841(3)	3297(2)	4550(3)	34(1)
N(2)	4579(3)	−82(3)	7393(3)	48(1)
C(1)	−420(3)	1679(2)	5349(3)	31(1)
C(2)	−692(3)	2643(2)	5610(3)	35(1)
C(3)	−1842(4)	2992(3)	3408(3)	46(1)
C(4)	369(4)	3462(3)	4230(4)	44(1)
C(5)	−1259(4)	4166(2)	4995(4)	45(1)
C(6)	2158(3)	51(3)	6729(3)	36(1)
C(7)	3380(4)	51(3)	7775(4)	46(1)
C(8)	4856(5)	701(4)	6674(5)	73(2)
C(9)	5638(4)	−174(4)	8597(4)	65(2)
C(10)	4522(5)	−940(3)	6663(4)	66(2)
Cl(2)	6008(1)	2121(1)	455(2)	776(6)
O(5)	3154(5)	2489(6)	−73(6)	201(4)
O(6)	2434(5)	2737(4)	2132(5)	139(3)

^{a}U_{eq} defined as one third of the trace of the orthogonalized U tensor.

TABLE 2. Selected bond lengths (Å) and bond angles (°)

Coordination geometry about Rh atom			
Rh(1)–Rh(1a)	2.413(1)	Rh(1)–Cl(1)	2.557(1)
Rh(1)–O(2)	2.035(2)	Rh(1)–O(4)	2.034(2)
Rh(1)–O(1a)	2.034(2)	Rh(1)–O(3a)	2.043(2)
Cl(1)–Rh(1)–O(2)	91.2(1)	Cl(1)–Rh(1)–O(4)	89.3(1)
O(2)–Rh(1)–O(4)	91.4(1)	Cl(1)–Rh(1)–Rh(1a)	176.4(1)
O(2)–Rh(1)–Rh(1a)	87.7(1)	O(4)–Rh(1)–Rh(1a)	87.4(1)
Cl(1)–Rh(1)–O(1a)	93.2(1)	O(2)–Rh(1)–O(1a)	175.6(1)
O(4)–Rh(1)–O(1a)	89.0(1)	Rh(1a)–Rh(1)–O(1a)	87.9(1)
Cl(1)–Rh(1)–O(3a)	95.4(1)	O(2)–Rh(1)–O(3a)	88.8(1)
O(4)–Rh(1)–O(3a)	175.3(1)	Rh(1a)–Rh(1)–O(3a)	87.9(1)
O(1a)–Rh(1)–O(3a)	90.5(1)		
Hydrogen bonding			
O(5)···Cl(2)	3.084(5)	O(5)···O(6)	2.814(5)
O(6)···Cl(1)	3.248(5)	O(6)···O(5b)	3.003(5)
Cl(2)··O(5)··O(6)	112.7(3)	Cl(2)··O(5)··O(6c)	97.5(3)
O(6)··O(5)··O(6c)	149.6(3)	Cl(1)··O(6)··O(5)	100.7(3)
Cl-(1)··O(6)··O(5b)	72.8(3)	O(5)··O(6)··O(5b)	146.4(3)

Symmetry transformation: a $(-x, -y, 1-z)$; b $(x, \frac{1}{2}-y, \frac{1}{2}+z)$; c $(x, \frac{1}{2}-y, -\frac{1}{2}+z)$.

factors were used, and anomalous dispersion corrections were incorporated [13]. The final positional parameters and equivalent isotropic thermal parameters of the non-hydrogen atoms are listed in Table 1, and selected bond lengths and angles in Table 2.

Results and discussion

The dinuclear cation has a tetra-bridged, barrel-like core (Fig. 1) with a crystallographic centre of inversion at the midpoint of the Rh–Rh bond. The Rh–Rh distance (2.413(1) Å) of this cation lies in the range 2.371(1)–2.486(1) Å for metal–metal single bonds in symmetrical $Rh_2(RCO_2)_4L_2$ complexes, and the mean Rh–O bond length (2.036(2) Å) is comparable to those found in the bridged carboxylato complexes [2]. The chloro ligands are axially bound to the $Rh_2(BET)_4$ cage at Rh–Cl = 2.557(1) Å. The present cation is structurally similar to known tetra(carboxylato)dirhodium complexes but electronically different from them. This difference arises from the overall electrical neutrality of betaine, as opposed to the more common anionic carboxylato ligands. Table 3 shows the influence of different charge distribution between ligands on the structure of symmetrical $Rh_2(RCO_2)_4L_2$ and related systems. For the three species with Cl^- anions in the axial positions (**2**, **4** and **5**), the inverse relationship between metal–metal and metal–axial ligand bond lengths is observed clearly. With bivalent carbonato anions as bridging ligands, hexaanion **4** has the shortest Rh–Rh and the longest Rh–Cl bonds; dianion **2**, bridged by univalent acetato anions, has the longest Rh–Rh and shortest Rh–Cl bonds; for the present complex (**5**), both intermediate Rh–Rh and Rh–Cl bond lengths are found. The dichloro complexes **5** and **4** possess $[Rh_2(BET)_4]^{4+}$ and $[Rh_2(CO_3)_4]^{4-}$ central fragments, respectively, and the high positive charge residing on the former undoubtedly contributes to a shortening of the Rh–Cl bond. For the two complexes containing axial aqua ligands (**1** and **3**), the inverse relationship

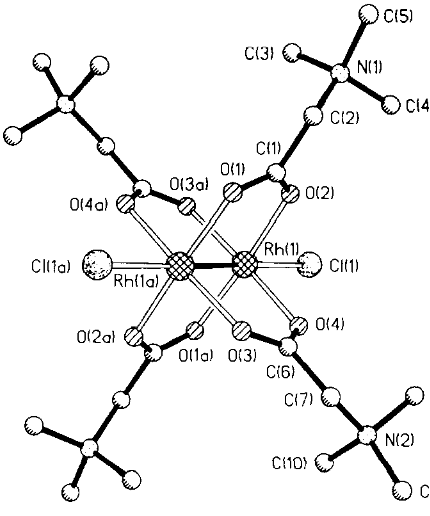

Fig. 1. Perspective view showing molecular structure of $[Rh_2(BET)_4Cl_2]^{2+}$ with atom numbering.

TABLE 3. Influence of different charge distribution of ligands on the structure of symmetrical $Rh_2(RCO_2)L_2$ and related species

No.	Species	M–M (Å)	M–L_{trans} (Å)	M–L_{eq} (av. Å)	Reference
1	$Rh_2(MeCO_2)_4(H_2O)_2$	2.3855(5)	2.310(3)	2.039(3)	14
2	$[Rh_2(MeCO_2)_4Cl_2]^{2-}$	2.47(1)	2.49(1)	2.06(1)	15
3	$[Rh_2(CO_3)_4(H_2O)_2]^{4-}$	2.378(1)	2.344(5)	2.033(5)	16
4	$[Rh_2(CO_3)_4Cl_2]^{6-}$	2.380(2)	2.601(3)	2.043(8)	16
5	$[Rh_2(BET)_4Cl_2]^{2+}$	2.413(1)	2.557(1)	2.037(2)	this work

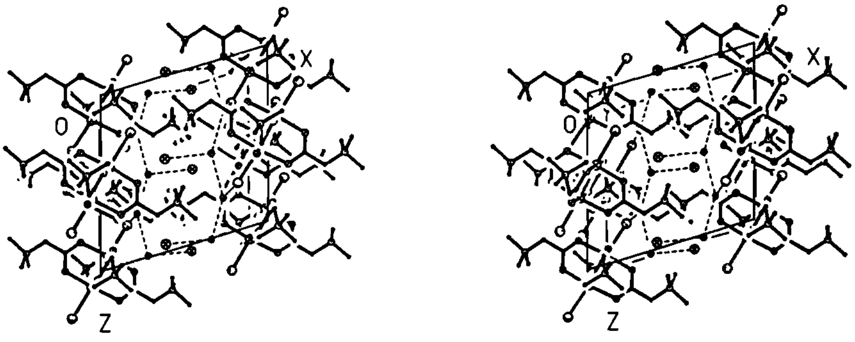

Fig. 2. Stereoview of the crystal structure of $[Rh_2(BET)_4Cl_2]Cl_2 \cdot 4H_2O$. The origin of the unit cell lies at the upper left corner, with *a* pointing from left to right in a slant, *b* towards the reader, and *c* downwards.

also holds, i.e. the slightly weaker Rh–O axial bond in the carbonato complex is matched with a slightly stronger Rh–Rh bond. From Table 3 it can be seen that the Rh–O equatorial bonds remain almost invariant in all complexes. In the present complex (**5**) the average Rh–O–C angle of 118.7(2)° is slightly less than that found in $Rh_2(OAc)_4(H_2O)_2$ (119.5(3)°) [14], while the average O–C–O angle (127.1(3)°) in the BET ligands is slightly greater than that in the acetato complex (124.8(3)°). Both of these angular variations are in accord with the longer Rh–Rh distance observed in the present dirhodium cation.

The crystal structure comprises discrete $[Rh_2(BET)_4Cl_2]^{2+}$ cations, chloride anions and water molecules. As illustrated in Fig. 2, the water molecules form a hydrogen-bonded zigzag chain in the direction of the *c* axis, and the chloro ligands and chloride ions are alternately attached to it by O–H···Cl hydrogen bonds in a 'herring-bone' manner. The water–chloride interactions (3.084(5) Å) are significantly stronger than the water–chloro ligand interactions; the geometrical details of the hydrogen bonding are given in Table 2. The resultant crystal structure is built of thick layers which match the (100) family of planes (Fig. 2).

The complex exhibits the following infrared absorption bands: ν(COO) at 1623vs, 1396s, and δ(COO) at 598m. The separation (Δ) between ν_{asym} and ν_{sym} is 227 cm^{-1}, which is significantly smaller than the value of 236 cm^{-1} for uncomplexed betaine [17] and hence indicative of the bidentate bridging mode of metal coordination.

Supplementary material

Additional materials comprising all bond lengths and angles, thermal parameters, H atom coordinates, and observed and calculated structure factor amplitudes (24 pages) are available from author T.C.W.M. on request.

References

1 X.-M. Chen and T. C. W. Mak, *J. Crystallogr. Spectrosc. Res.*, in press.
2 F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, Wiley, New York, 1982.
3 F. A. Cotton and R. A. Walton, *Struct. Bonding (Berlin)*, *62* (1985) 1.
4 R. M. Norman and H. J. Kolari, *J. Am. Chem. Soc.*, *100* (1978) 791.
5 F. M. O'Neill and J. C. A. Boeyens, *Inorg. Chem.*, *29* (1990) 1302.
6 G. G. Christoph and Y.-B. Koh, *J. Am. Chem. Soc.*, *101* (1979) 1422.
7 F. A. Cotton and T. R. Felthouse, *Inorg. Chem.*, *19* (1980) 323.
8 T. C. W. Mak, *J. Mol. Struct.*, *220* (1990) 13.
9 G. A. Rempel, P. Legzdins, H. Smith and G. Wilkinson, *Inorg. Synth.*, *13* (1972) 90.

10 R. Diamond, *Acta Crystallogr., Sect. A, 25* (1969) 43.
11 G. Kopfmann and R. Huber, *Acta Crystallogr., Sect. A, 24* (1968) 348.
12 G. M. Sheldrick, in G. M. Sheldrick, C. Krüger and R. Goddard (eds.), *Crystallographic Computing 3: Data Collection, Structure Determination, Protein, and Databases*, Oxford University Press, New York, 1985, p. 175.
13 J. A. Ibers and W. C. Hamilton (eds.), *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, U.K., 1974, pp. 55, 99, 149.
14 F. A. Cotton, B. G. De Boer, M. D. LaPrade, J. R. Pipal and D. A. Ucko, *Acta Crystallogr., Sect. B, 27* (1971) 1664.
15 E. M. Shustorovich, M. A. Porai-Koshits and Yu. A. Buslaev, *Coord. Chem. Rev., 17* (1975) 1.
16 F. A. Cotton and T. R. Felthouse, *Inorg. Chem., 19* (1980) 320.
17 K. M. Harmon and G. F. Avci, *J. Mol. Struct., 117* (1984) 295.