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TRIPLY BRIDGED THIOBENZOATO CARBONYL MANGANATES(I) AND RHENATES(I). THE CRYSTAL AND MOLECULAR STRUCTURE OF CAESIUM TRIS(μ-THIOBENZOATO(S))BIS(TRICARBONYL RHENATE) *

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Summary

By reaction of potassium or caesium monothiobenzoate (mtb) with manganese or rhenium pentacarbonyl bromide the binuclear triply S-monothiobenzoato bridged complexes $[(CO)_3M(\mu\text{-mtb})_3M(CO)_3]^-$ have been obtained as salts. The title compound crystallizes in the orthorhombic space group $P2_12_12_1$ with a 15.239(6), b 15.234(6), c 15.209(6) Å and $Z = 4$. The Re atoms are octahedrally coordinated. The two octahedra share a common face. The rhenium atoms are not equivalent with respect to their bonds to the thiobenzoato ligands, leading to two sets of Re—S bond lengths, 2.545(4) and 2.504(5) Å.

Introduction

Metal complexes of the monothiobenzoate (mtb) ligand show various stereochemistries. Besides chelating bidentate, the bifunctional unsymmetric ligating group may also effect binuclear complexes [1—5]. Coordination may occur also through sulfur only in a unidentate or bridging manner [6]. Hieber and coworkers [7,8] already reported mtb complexes of manganese and rhenium: the mononuclear O, S chelated $(CO)_4$Mn mtb and the dinuclear bis(thiobenzoato) bridged $[(CO)_4\text{Re mtb}]_2$. To get these compounds they treated the respective carbonyl halides with thiobenzoic acid in tetrahydrofuran or benzene. We reinvestigated these reactions as part of a more general study of reactions between low valent transition metals and ambivalent O,S donor ligands [9]. Using ethanol as solvent and potassium or caesium monothiobenzoate instead of the free acid we obtained the new dimeric complex anions $[(CO)_3M(mtb)_3M(CO)_3]^-$, M = Mn, Re, as potassium or caesium salts. Few thiobenzoato com-

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* Dedicated to Professor E.G. Rochow on the occasion of his 70th birthday.

plexes and very few dimer metal carbonyl derivatives, consisting of two face-sharing octahedra, have been characterized structurally so far. In this paper the isolation, the crystal and molecular structure, and vibrational spectra of these new compounds are described.

Experimental

All reactions were performed under dry, prepurified nitrogen. All solvents were dried before use. Infrared spectra were recorded on a Perkin—Elmer 225 spectrometer as KBr pellets and in the carbonyl-stretching region using acetone as solvent. Microanalysis was performed by standard techniques with exception of Mn and Re, for which atomic absorption spectrometry was used.

Preparation of potassium tris(μ-thiobenzoato)bis(tricarbonyl manganate)

A solution of 200 mg (0.727 mmol) $Mn(CO)_5Br$ and 195 mg Kmtb in ethanol was stirred for 1 h at 80—85° C. The solution turned dark red. After cooling to —20° C KBr was filtered off. The solvent was removed at reduced pressure affording 60 mg of the product. Recrystallization from ethanol yielded a red microcrystalline solid. Anal.: Found: C, 44.12; H, 2.67; Mn, 14.2; S, 12.3. $C_{27}H_{15}KMn_2O_9S_3$ calcd.: C, 44.50; H, 2.06; Mn, 15.1; S, 13.2%.

The caesium salts and the respective rhenates have been prepared by similar procedures. $Re(CO)_5Br$ was reacted for 7 h. $Cs[(CO)_3Re(mtb)_3Re(CO)_3]$ is a bright yellow crystalline compound. Anal.: Found: C, 30.6; H, 1.90; Cs, 14.0; Re, 35.0; S, 8.73; $C_{27}H_{15}O_9CsRe_2S_3$ calcd.: C, 29.9; H, 1.28; Cs, 12.3; Re, 34.3; S 8.35%.

Single-crystal X-ray data

$C_{27}H_{15}CsRe_2O_9S_3$, mol. wt. 1084, yellow orthorhombic crystals, space group $P2_12_12_1$, with cell constants a 15.239(6), b 15.234(6), c 15.209(6) Å; V 3530.8 Å^3; D_m 2.10(2) (by flotation), D_c 2.04 g cm^{-3} for $Z = 4$, $F(000) = 2008$, μ 85.0 cm^{-1} (Mo-K_α).

Intensity measurement. Solution of the structure

A single crystal of the approximate dimensions 0.3 × 0.5 × 0.2 mm was mounted on a Syntex $P2_1$ four circle diffractometer. The intensities were collected up to 2ϑ equal 54° by a 7 step ω-scan with variable scan speed (3.91—29.3° /min). The ratio of scan time to background counting was 0.5. From 4322 reflections measured, 2732 independent reflections had a ratio $\sigma(I)/I >$ 0.51. They were used in the refinement. The structure was solved by "direct methods". The refinement was carried out by full-matrix least-squares with all atoms treated anisotropically with the exception of the phenyl carbon atoms. Hydrogen atoms were not included. The final values of the conventional R and R_w indices were 0.063 and 0.061. The weighting scheme $1/w = \sigma(F_0)^2 + (0.02\ F_0)^2$ was used throughout the refinement. The rhenium and caesium form factor was corrected both for the real and imaginary part of the anomalous dispersion. The absolute configuration could be fixed (R value of the inverse structure, 0.079). The results of the refinements are reported in Table 1. All computations were performed on a Data General Eclipse using the Syntex E-XTL system.

Results and discussion

Kmtb or Csmtb react in ethanol at 80—85° C with manganese or rhenium pentacarbonyl bromide as follows:

$$2\ M(CO)_5Br + 3\ Kmtb \rightarrow [(CO)_3M(mtb)_3M(CO)_3]^- + K^+ + 2\ KBr + 4\ CO$$
$$M = Mn, Re.$$

The complex ions are formed in high yield. No other product, e.g. $(CO)_4Mn$ mtb [7] or $[CO)_4Re\ mtb]_2$ [8] could be isolated. Obviously, the formation of an insoluble salt plays an important role in determining the kind of the reaction product. The salts of the dinuclear anions are air stable compounds, soluble in polar, insoluble in nonpolar solvents. The stoichiometry suggests a dinuclear complex ion, consisting of two octahedra sharing a face. Bridging may be effected through 3 unidentate thiobenzoate ligands coordinated through sulfur. Accordingly, ν(CO) of the mtb ligand is raised to 1640 cm^{-1}, compared to 1500 cm^{-1} in Kmtb. The strong band at 1200 cm^{-1} is assigned to ν(phenyl-C). This band remains unchanged in Kmtb indicating that the monothiocarboxylato group is not conjugated with the phenyl ring, in constrast to the dithiobenzoate ligand [10]. The two strong bands at 950 and 680 cm^{-1} are lowered in the complex, to 894 and 664 cm^{-1}, caused by the monodentate bonding sulfur. These frequencies are highly coupled modes of a phenyl ring deformation coordinate and the ν(CS) coordinate [10,11].

In the carbonyl stretching frequency range 4 bands are observed for the solid state, at 2031m, 2011vs, 1924vs and 1902vs cm^{-1}. The two sharp bands at higher wave numbers have to be assigned to the symmetric stretching modes, the two bands at lower wave numbers to the antisymmetric stretching modes of the two $Re(CO)_3$ groups. Obviously, the splitting into 4 bands reflects a different bonding of the rhenium atoms to the ligands. In solution, however, only two bands are found, at 2011vs and 1912vs cm^{-1}. This means, that in solution the two rhenium atoms are equivalent and the $(CO)_3ReS_3Re(CO)_3$ core of the complex ion has D_{3h} symmetry.

The X-ray work at the rhenium compound confirmed the structure model already described. In the dinuclear anion (see Fig. 1) the two $Re(CO)_3$ groups are connected by three bonds through the sulfur atoms of three monodentate mtb ligands. The anion itself deviates hardly from C_3 symmetry. The $(CO)_3Re-S_3Re(CO)_3$ core alone has symmetry close to C_{3v}. The Re—Re distance is 3.404(2) Å. There are two sets of Re—S distances. Re(1) has a mean distance of 2.545(4) Å to three sulfur atoms, whereas the Re(2)—S distances, mean value 2.504(5) Å, are significantly shorter by 0.041(5) Å. The two Re atoms are not equivalent with respect to their bonding to the mtb ligands. Re(2) lies clearly in the planes through the C, O, S atoms of all mtb ligands. Re(1) is situated nearly at right angles to these planes.

A possible explanation for the different Re—S bond lengths is, that the shorter Re—S bond contains some π character, which results from electron delocalization within the thiocarboxyl group. The σ overlap can be equal in both bonds, because the Re—S—C angles do not differ greatly. The structural parameters found for the sulfur bridged dinuclear manganese complexes with four or five membered chelate rings, di-μ-N-methylimino(methylthio)methane-

(Continued on p. 196)

TABLE 1

FINAL POSITIONAL AND THERMAL PARAMETERS OF $[(CO)_3Re(\mu\text{-mbt})_3Re(CO)_3]^-$

	$x \times 10^4$	$x \times 10^4$	$z \times 10^4$	$B_{11}(B)$	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Re(1)	2561(1)	2441(1)	2560(1)	3.0(0)	3.5(0)	3.1(0)	0.3(0)	−0.2(0)	0.3(0)
Re(2)	3851(1)	1150(1)	3851(1)	4.1(1)	4.6(1)	4.2(0)	0.9(0)	−0.9(0)	0.9(1)
Cs	6274(1)	3729(2)	3725(1)	6.1(1)	7.0(1)	6.3(1)	1.0(1)	0.8(1)	−0.8(1)
S(1)	4189(4)	2077(4)	2534(5)	3.3(3)	4.0(3)	4.3(3)	0.4(2)	0.1(3)	−0.1(3)
S(2)	2536(5)	0811(4)	2921(4)	4.4(3)	3.7(3)	3.5(3)	0.5(3)	0.0(3)	0.7(2)
S(3)	2926(4)	2453(5)	4195(4)	3.6(3)	4.1(3)	3.2(3)	−0.4(3)	−0.4(2)	0.2(3)
O(1)	0635(13)	2842(14)	2927(14)	3.4(0)	6.5(12)	5.6(11)	1.3(9)	0.6(9)	−0.5(9)
O(2)	2175(4)	2084(15)	0642(13)	5.5(12)	8.1(14)	3.5(10)	−0.3(10)	−0.7(9)	−0.7(10)
O(3)	2915(17)	4358(16)	2175(17)	7.3(14)	5.0(11)	7.9(16)	−1.3(11)	−0.9(12)	0.5(12)
O(4)	3197(23)	0164(25)	5482(23)	10.1(23)	14.4(28)	8.9(21)	−2.1(20)	−1.1(19)	3.8(21)
O(5)	5475(17)	1815(18)	4848(16)	6.4(14)	8.6(17)	11.7(21)	3.2(14)	−4.5(15)	−1.6(15)
O(6)	4805(21)	−0495(20)	3222(23)	10.4(21)	7.4(16)	12.1(23)	1.4(17)	−1.6(17)	2.9(18)
O(7)	4211(16)	0637(14)	1613(14)	8.3(15)	4.8(11)	6.3(11)	0.1(11)	0.4(11)	−0.7(10)
O(8)	1594(15)	0804(16)	4374(14)	6.1(12)	9.0(16)	3.6(10)	−0.5(12)	0.3(10)	1.2(11)
O(9)	4364(14)	3400(15)	4189(14)	4.4(11)	8.0(14)	6.0(13)	−0.3(11)	−0.8(10)	−0.3(11)
C(1)	1371(16)	2663(20)	2768(18)	2.4(11)	6.9(18)	4.8(14)	−1.2(12)	0.3(10)	−2.0(14)
C(2)	2303(15)	2243(19)	1364(18)	5.3(17)	5.6(16)	3.4(13)	−2.4(13)	−0.9(12)	1.2(11)
C(3)	2790(17)	3580(27)	2318(16)	3.0(12)	10.6(27)	1.7(11)	−0.2(15)	−0.6(5)	0.1(14)
C(4)	3513(24)	0531(29)	4825(31)	4.6(19)	8.5(27)	9.8(33)	0.2(19)	−4.7(22)	−3.4(26)
C(5)	4876(26)	1520(27)	4451(25)	7.6(24)	9.0(26)	5.4(20)	4.5(22)	−1.5(18)	−0.1(19)
C(6)	4405(30)	0164(25)	3461(25)	12.2(32)	7.4(23)	7.5(23)	−7.8(23)	−6.2(23)	7.8(21)
C(7)	4267(18)	1402(18)	1547(18)	4.2(14)	3.0(13)	3.6(13)	0.2(11)	0.9(11)	−0.9(11)
C(8)	4470(20)	1885(19)	0713(20)	4.3(6)					
C(9)	4726(19)	2756(19)	0744(20)	4.8(7)					
C(10)	4964(23)	3173(24)	−0069(25)	6.7(9)					
C(11)	4886(21)	2681(22)	−0876(22)	6.2(8)					
C(12)	4616(28)	1774(26)	−0931(29)	8.7(11)					
C(13)	4371(21)	1403(21)	−0076(21)	5.5(7)					
C(14)	1570(19)	0727(18)	3596(21)	4.3(14)	4.1(14)	4.6(16)	−1.0(12)	0.3(13)	−0.8(12)
C(15)	0740(19)	0572(19)	3138(18)	4.1(6)					
C(16)	0736(21)	0289(20)	2241(20)	5.2(7)					
C(17)	−0095(25)	0036(22)	1837(25)	6.7(9)					
C(18)	−0898(21)	0084(20)	2342(22)	5.9(8)					
C(19)	−0890(28)	0390(26)	3212(26)	8.1(11)					
C(20)	−0063(21)	0664(21)	3593(22)	5.6(8)					
C(21)	3574(17)	3442(19)	4248(17)	2.5(12)	5.6(15)	3.2(13)	−1.1(11)	−0.2(10)	−1.5(11)
C(22)	3123(20)	4284(21)	4471(21)	4.9(7)					
C(23)	2227(18)	4267(18)	4718(18)	4.1(6)					
C(24)	1822(25)	5138(25)	4952(23)	6.8(9)					
C(25)	2310(25)	5865(24)	4927(23)	7.1(9)					
C(26)	3227(24)	5911(25)	4605(25)	7.2(9)					
C(27)	3573(23)	5049(22)	4391(23)	6.1(8)					

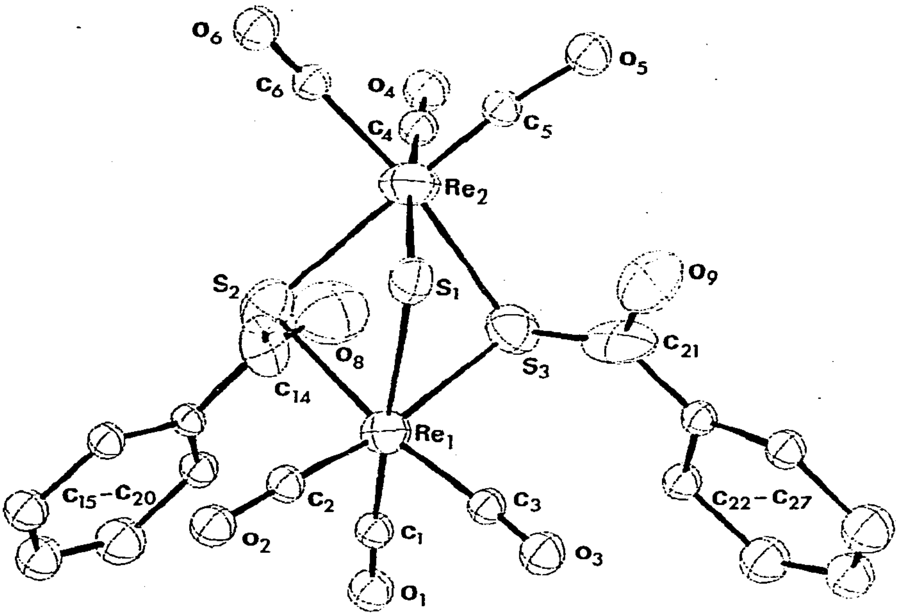

Fig. 1. ORTEP-plot of [(CO)$_3$Re(μ-mtb)$_3$Re(CO)$_3$)]$^-$. One CO—C$_6$H$_5$ group (at (S(1)) has been ommitted for clarity.

TABLE 2

BOND DISTANCE (Å) AND BOND ANGLES (deg.) WITHIN [(μ-mtb)$_3$Re$_2$(CO)$_6$]$^-$

Re(1)—S(1)	2.543(6)	S(1)—Re(2)—S(2)	80.2(2)
Re(1)—S(2)	2.543(6)	S(1)—Re(2)—S(3)	80.3(2)
Re(1)—S(3)	2.548(6)	S(2)—Re(1)—S(3)	80.3(2)
Re(1)—C(1)	1.87(2)		
Re(1)—C(2)	1.88(3)	S(1)—C(7)—O(7)	119(3)
Re(1)—C(3)	1.81(4)	S(2)—C(14)—O(8)	123(3)
		S(3)—C(21)—O(9)	119(3)
C(7)—O(7)	1.17(3)		
C(14)—O(8)	1.19(4)	Re(2)—S(2)—C(14)	111(1)
C(21)—O(9)	1.21(3)	Re(2)—S(2)—C(14)	110(1)
C(7)—C(8)	1.50(4)	Re(2)—S(3)—C(21)	111(1)
C(14)—C(15)	1.48(4)		
		S(1)—Re(1)—S(2)	78.7(2)
Re(2)—S(1)	2.504(8)	S(1)—Re(1)—S(3)	78.7(2)
Re(2)—S(2)	2.506(8)	S(2)—Re(1)—S(3)	78.8(2)
Re(2)—S(3)	2.502(7)		
Re(2)—C(4)	1.83(4)	Re(1)—S(1)—Re(2)	84.8(2)
Re(2)—C(5)	1.89(4)	Re(1)—S(2)—Re(2)	84.8(2)
Re(2)—C(6)	1.82(4)	Re(1)—S(3)—Re(2)	84.8(2)
S(1)—C(7)	1.82(3)	Re(1)—S(1)—C(7)	101(1)
S(2)—C(14)	1.80(3)	Re(1)—S(2)—C(14)	102(1)
S(3)—C(21)	1.79(3)	Re(1)—S(3)—C(21)	100(1)
C(21)—C(22)	1.49(4)		
Re(1)—Re(2)	3.404(2)		

thiolatobis(tricarbonylmanganese), $[Mn_2(CO)_6(\mu\text{-}SC(SMe))_2]$ [12] and di-μ-*S*-(*S*-methyl-*N*-isopropylidenedithiocarbazate(*N*,*S*))bis(tricarbonylmanganese), $[Mn_2(CO)_6(\mu\text{-}(CH_3)_2CNNCSSCH_3)_2]$ [13] show also, that the Mn—S bond distances in the ligand planes are significantly smaller than the bonds at right angles (by 0.063(8) and 0.023(1) Å, respectively). This supports the above arguments. However, in di-μ-mercaptobenzothiazolato(*N*,*S*)bis(tricarbonylrhenium), $[Re_2(CO)_6(\mu\text{-}C_6H_4NCS_2)]_2$ [14] the Re—S bond lengths at right angles to the ligand planes are the smaller ones, although the bond angles at the sulfur atom are very similar to the forementioned methyliminomanganese complex. The situation is, therefore, not yet completely clear.

In the present compound, the size of the Re—S—Re bond angles is highly determined by the repulsive forces between the sulfur atoms. The mean S ··· S non-bonding distance is only 3.23(1) Å. The remaining bond lengths and angles have rather high standard deviations, and are therefore not discussed in detail. The phenyl rings of the ligands are not coplanar with the thiocarboxylato groups; the three torsional angles are close to 12°. Similar values have been found in $[Ni(mtb)_2C_2H_5OH]$ [2,3]. Conjugation through the OSC—phenyl ring bond may not be possible, as, for instance, in dithiobenzoato complexes [15], where the whole ligand is planar. By examination of the vibrational spectra the same conclusions were obtained for both ligands [10]. The bonding of the thiobenzoato ligands just described effects that in the solid state all three phenyl groups are directed to the same side of the dinuclear complex ion (see Fig. 1). The three-dimensional structure is based on a cubic close-packing of the anions. This is demonstrated by the pseudo cubic cell dimensions and the specific coordinates of Re(1), Re(2) and Cs. Caesium is coordinated to three oxygen atoms only (mean distance 3.03(2) Å). According to powder diagrams all compounds synthetized are isostructural.

The present compounds belong to a rare species of dinuclear complexes. Other examples are $[N(C_2H_5)_4]_3[(CO)_3M(\mu\text{-}Cl)_3M(CO)_3]$ with M = Mo, W [16] and $[N(C_2H_5)_4][(CO)_3Re(OCH_3)_3Re(CO)_3]$ [17].

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