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POLYNUCLEAR CARBONYL COMPLEXES OF RUTHENIUM AND OSMIUM WITH METHYLTHIOLATE AND BROMIDE BRIDGING LIGANDS

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The reactions of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ with $(CH_3S)_2$ give polymeric $[Ru(SCH_3)_2(CO)_2]_n$, (n = 242) and $[Os(SCH_3)_2(CO)_2]_n$, (n = 34). The polymers react with bromine to form binuclear derivatives, $[MBr(SCH_3)_2(CO)_2]_2$, (M = Ru, Os). The i.r. and x-ray photoelectron data, and the possible structures are reported.

Sulfur-bridged dimeric iron complexes $[FeSR(CO)_3]_2$ are formed by the reactions of $Fe_3(CO)_{12}$ with organic thiols, sulfides or disulfides.1) Preparations and infrared spectra of thiolato carbonyl ruthenium compounds were first reported by Johnson *et al.*,2) who obtained the compounds $[Ru(SR)_2(CO)_2]_n$ (R = CH_3, C_2H_5, n-C_4H_9, C_6H_5) from the reactions of triruthenium dodecacarbonyl and thiols. These compounds are similar to the polymeric halides $[RuX_2(CO)_2]_n$ which are believed to have a halogen-bridged chain structure with *cis* carbonyl groups.3) However, no information is available about the analogous compound of osmium and the polymerization number n. We report here preparations and properties of the polynuclear compounds $[M(SCH_3)_2(CO)_2]_n$ and their bromine derivatives $[MBr(SCH_3)_2(CO)_2]_2$, (M = Ru and Os).

A mixture of 0.5 g $Ru_3(CO)_{12}$ and 1.5 ml methyl disulfide was stirred in benzene at reflux under nitrogen. The starting orange solution changed to red with gas evolution and then yellow. After 6 h, 10 ml of pentane was added to the reddish yellow solution. The resulting orange ocher precipitates were collected by filtration. The compound was recrystallized from benzene-pentane (2:1), and dried *in vacuo*; yield 75%. Found: C, 19.40; H, 2.17; O, 12.45; S, 24.63; Ru, 40.91%. Calcd for $[Ru(SCH_3)_2(CO)_2]_n$; C, 19.12; H, 2.41; O, 12.73; S, 25.52; Ru, 40.22%. The average molecular weight (M = 60800±700) was determined at 40°C using a Corona 117 molecular weight apparatus, and then the average value of n was evaluated to be 242. The n.m.r. spectrum of this compound in C_6D_6 solution was found to exhibit a single broad peak for the methyl proton at δ = 2.35 p.p.m.

A mixture of 0.7 g $Os_3(CO)_{12}$ and 1.5 ml $(CH_3S)_2$ was refluxed in 15 ml toluene under nitrogen. After 25 h, 15 ml of ether was added to the dark yellow solution. The resulting ocher precipitates were collected by filtration. The compound was recrystallized from toluene-ether (1:1), and dried *in vacuo*; yield 75%. Found; C, 14.57; H, 2.01; O, 9.12; S, 18.48%. Calcd for $[Os(SCH_3)_2(CO)_2]_n$; C, 14.11; H, 1.78; O, 9.40; S, 18.84%. From the average molecular weight (11500±400) measured at 40°C using a benzene solution of complex, the average value of n was determined to be 34. The n.m.r. spectrum of this compound in $CDCl_3$ exhibits a single broad peak for the methyl proton at δ = 2.68 p.p.m.

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Benzene solution of bromine (0.08 g) was added dropwise to a benzene solution of $[Ru(SCH_3)_2(CO)_2]_n$ (0.251 g) and $[Os(SCH_3)_2(CO)_2]_n$ (0.34 g), respectively, in a cooling bath. The solution, which had darkened, was pumped to dryness, dissolved in a minimum amount of benzene, and the product was precipitated by the addition of n-pentane. Orange-brown ruthenium product and dark ocher osmium product was respectively filtered off, washed with pentane, and dried under vacuum.

Bromine derivative of ruthenium compound. Found; C, 14.12; H, 1.81; S, 19.70%. Calcd for $[RuBr(SCH_3)_2(CO)_2]_2$; C, 14.51; H, 1.83; S, 19.36%. The molecular weight of 665 measured by the osmometric method using a chloroform solution agreed with the calculated value 662.3. The n.m.r. spectrum of this compound in $CDCl_3$ was found to exhibit two methyl proton resonances at δ = 2.43 and δ = 2.70 p.p.m.

Bromine derivative of osmium compound. Found; C, 11.71; H, 1.61; S, 14.91%. Calcd for $[OsBr(SCH_3)_2(CO)_2]_2$; C, 11.43; H, 1.44; S, 15.26%. The molecular weight of 848 measured by the osmometric method is quite close to the calculated value, 840.6. The n.m.r. spectrum of this compound in $CDCl_3$ exhibits a single broad peak for the methyl proton at δ = 2.77 p.p.m.

The x-ray photoelectron spectra were recorded using an AEI ES 100B spectrometer (Al K_α radiation) with a cold probe (ca. -95°C). The measured binding energies were standardized using a C 1s binding energy of 285.0 eV. The data are summarized in Table 1 with those of reference samples.

Table 1. Metal and sulfur core electron binding energies of metal complexes

Complex	Binding energy / eV	
	Ru $3d_{5/2}$, (±0.4 eV)	S $2p_{3/2}$, (±0.2 eV)
$[Ru(SCH_3)_2(CO)_2]_n$	279.9	163.0
$[RuBr(SCH_3)_2(CO)_2]_2$	282.2	163.7
Ru metal	279.2	——
$[RuN_2(NH_3)_5]I_2$	281.1	——
$RuCl_3 \cdot 3H_2O$	282.3	——
$BaRuO_4$	284.4	——
	Os $4d_{5/2}$, (±0.4 eV)	
$[Os(SCH_3)_2(CO)_2]_n$	280.1	163.1
$[OsBr(SCH_3)_2(CO)_2]_2$	281.1	164.0
K_2OsO_4	283.8	——

The spectra of various ruthenium and osmium compounds show an increase of the Ru $3d_{5/2}$ or Os $4d_{5/2}$ binding energy with increasing a formal oxidation state. From the values of Ru $3d_{5/2}$ and Os $4d_{5/2}$ binding energies, the metals in the polynuclear and binuclear compounds were respectively estimated to be in the formal oxidation states II and III except for $[Ru(SCH_3)_2(CO)_2]_n$. The value for this complex is lower than predicted for the oxidation state II and it requires further examination. The S $2p_{3/2}$ binding energies for the polynuclear compounds are found to be in good agreement with those for

$[Fe(SCH_3)(CO)_3]_2$ and $[Fe(SC_2H_5)(NO)_2]_2$ and this supports the observation that bridging thiol groups generally have S $2p_{3/2}$ binding energies close to 163 eV.[4] The values of S $2p_{3/2}$ binding energies for the Ru(III) and Os(III) compounds are larger than those for the polynuclear Ru(II) and Os(II) compounds. The alterations in S $2p_{3/2}$ binding energies were 0.7 eV and 0.9 eV per a unit charge on the metal for ruthenium and osmium compounds, respectively.

The infrared spectra of the ruthenium and osmium compounds recorded on a Perkin Elmer 325 spectrometer are shown in Table 2.

Table 2. Infrared data of $[M(SCH_3)_2(CO)_2]_n$ and $[MBr(SCH_3)_2(CO)_2]_2$ (M = Ru, Os)

Complex	$\nu_{co}(cm^{-1})^a$	$\nu_{co}(cm^{-1})^b$	Other bands $(cm^{-1})^b$
$[Ru(SCH_3)_2(CO)_2]_n$	2097vw	2098vw	1425s, 1303s, 1165w, 1140w, 1087w,
	2026vs	2025vs	1040w, 951s, 725m, 691w, 599s, 567s,
	1962vs	1962vs	500s, 470w, 443w, 327m, 301w, 272w
	1928vw	1931w	
$[RuBr(SCH_3)_2(CO)_2]_2$	2062vs	2058vs	1420s, 1305m, 1148sh, 1085m,br,
	1996s	1998vs	953s, 717w,br, 676w, 591m, 554s,
			487m, 425w,sh, 375w, 337w,sh, 280w
$[Os(SCH_3)_2(CO)_2]_n$	2097w	2099w	1425s, 1307s, 1256vw, 1170w, 1125m,br,
	2013vs	2015vs	1025vw, 953s, 718vw, 699vw, 616s,
	1945vs	1950vs	582s, 518s, 483w, 449vw, 326w, 297w,
	1911vw	1915w,sh	273vw
$[OsBr(SCH_3)_2(CO)_2]_2$	2109w	2110w	1423s, 1310m, 1257m, 1163w,sh, 1100s,br,
	2030s	2030s	1032w,sh, 967s, 730w, 678m, 612m, 577s,
	1962s	1960s	500m, 477m, 375w, 300w,sh

[a] Tetrahydrofuran. [b] Nujol. s = Strong, m = medium, w = weak, br = broad, sh = shoulder, v = very

For all the complexes, the presence of two strong carbonyl stretching frequencies indicates that the two carbonyl groups occupy *cis* position. There is no significant difference between the spectra measured in tetrahydrofuran and a Nujol mull. This suggests that the structures of the complexes in THF are similar to those in a mull state. A series of bands in the 1425 - 676 cm^{-1} region, are characteristic of SCH_3 ligand but several shifts provide an evidence of its coordination. It has been generally established that M-CO bending [δ(MCO)] and MC-stretching [ν(MC)] vibrations are present in the regions 700 - 500 cm^{-1} and 500 - 300 cm^{-1} for simple metal-carbonyl compounds and the ν(MC) decreases as the ν(C-O) increases.[5] Thus, the following assignments have been made for the poly- and bi-nuclear complexes: δ[Ru(II)CO], 599 and 567 cm^{-1}; ν[Ru(II)C], 500, 470, and 443 cm^{-1}; δ[Ru(III)CO], 591 and 554 cm^{-1}; ν[Ru(III)C], 487 and 425 cm^{-1}; δ[Os(II)CO], 616 and 582 cm^{-1}; ν[Os(II)C], 518, 483, and 449 cm^{-1}; δ[Os(III)CO], 612 and 577 cm^{-1}; ν[Os(III)C], 500 and 477 cm^{-1}. Adams and Chandler[6] have found that sulfur-bridged platinum(II) complex, $Pt_2Cl_4(SC_2H_5)_2$ exhibits $\nu(PtCl_t)$, (t = terminal) and ν(PtS) at 365 - 325 and 422 - 401 cm^{-1}, respectively, whereas halogen-bridged palladium(II) complex, $Pd_2Cl_4(SC_2H_5)_2$ exhibits $\nu(PdCl_t)$, $\nu(PdCl_b)$, (b = bridging), and ν(PdS) at 366, 266, and 358 cm^{-1}, respectively. Thus, ν(RuS) and ν(OsS) are tentatively assigned to 327 and 326 cm^{-1}, respectively for the type of $[M(SCH_3)_2(CO)_2]_n$ compound, whereas ν(RuBr) and ν(OsBr) are tentatively assigned to 375 cm^{-1} for the $[MBr(SCH_3)_2(CO)_2]_2$ complexes.

The proposed structures are shown in Figure for two kinds of complexes. The structure (I) and (II) are respectively analogous to that suggested for $[Mo(NO)_2Cl_2]_n$ 3) and for $[MX(CO)_4]_2$, (M = Mn, Tc, and Re; X = Cl, Br, and I). 7)

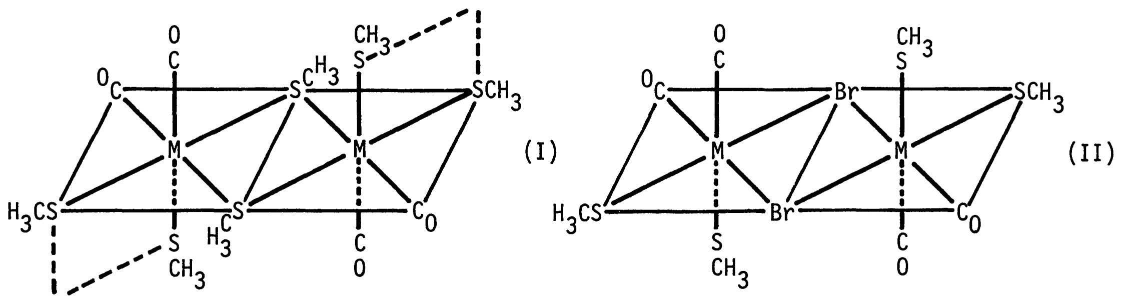

Figure. The possible structures of $[M(SCH_3)_2(CO)_2]_n$ (I) and $[MBr(SCH_3)_2(CO)_2]_2$ (II), (M = Ru, Os).

The mechanism by which the polymeric methylthiolato complexes are formed is of interest. The reactions of dodecacarbonyl triruthenium and triosmium with thiols proceed *via* a two-stage process involving (1) the formation of a cyclic Lewis-acid-base intermediate $M_3(H\text{-}SR)(CO)_{12}$, and (2) a subsequent rearrangement involving the cleavage of metal-metal and S-H bonds. 8) The reactions of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ with $(CH_3S)_2$ possibly follow a similar reaction path but both the cyclic intermediate $M_3(CH_3S\text{-}SCH_3)(CO)_{12}$ and linear $M_3(SCH_3)_2(CO)_{12}$ complexes are considered to be unstable to give *cis*-$M(SCH_3)_2(CO)_4$ which may lose carbon monoxide and polymerize to $[M(SCH_3)_2(CO)_2]_n$. This mechanism is consistent with the fact that $Ru_3(CO)_{12}$ reacts more rapidly with methyl disulfide than $Os_3(CO)_{12}$ because the metal-metal bond is stronger in the latter metal carbonyl.

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